ELECTROCHEMISTRY

and

ELECTROCHEMICAL ANALYSIS

A Theoretical and Practical Treatise
for Students and Analysts

BY

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VOLUME III

ELECTRICAL METHODS APPLIED TO TITRATION,
MOISTURE DETERMINATION AND p_H MEASUREMENT

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PREFACE

The present volume completes my treatise on Electrochemistry and Electrochemical Analysis. As explained in the Preface to Vol. I, its inception is due to the realization that the principles of Vol. I and the apparatus of Vol II are applicable also to branches of electrochemical analysis other than those which form the main subject-matter of Vol. II.

In fixing the scope of this book it was primarily my aim to give analysts as complete a survey of electrochemical methods and principles as possible, so as to enable them to choose for themselves such tests as may be applicable to their special problems. The conductimetric titration of extremely dilute solutions, the determination of moisture by capacitance measurements and the potentiometric determination of p_{π} are instances in point.

An equally important aim, however, is that of giving to students of Electrochemistry a grounding in the principles and practice of their science. I do not think that a better method can be found than the intelligent performance of the many exercises arising out of electrochemical analysis, most of which can be carried out with the apparatus described in Vol. II. In the present volume I have also devoted much attention to the discussion of theoretical principles and, as in Vol. I, I have frequently deviated from the current exposition of other books.

It is a pleasure to record my thanks to Dr. A. R. Martin, who has kindly written for me a great part of the section dealing with the determination of moisture by capacitance measurements.

HENRY J. S. SAND.

Newbury, *July*, 1941.

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Potentiometric Analysis

CHAPTER I

THEORETICAL CONSIDERATIONS

The Equivalence Point.

Potentiometric analysis forms a branch of volumetric analysis in which the end-point of a titration is detected by potentiometric means. As in other branches of volumetric analysis titrate ions are removed from the solution by the titrant either in the form of insoluble or of indifferent compounds, or else they may be converted into ions of a different kind, as when ferrous are oxidized to ferric, or cyanide are changed into argenticyanide ions. An **indicator** and a **reference electrode** are required. The former is an electrode which responds to changes in the concentration of the titrate ions, the latter, one that is unaffected by such concentration. As an illustration we take a silver solution, in which titrate silver ions are being removed by titrant chloride ions. A silver indicator electrode placed in such a solution at ordinary temperature becomes more negative by 0·058 volt, whenever the ionic concentration of the silver is reduced to one-tenth of its value. In the general case of an electrode reaction represented by equation $C15$ or $C15a$ (Vol. I, p. 76), electrode potential in its dependence on ionic concentrations is governed in a more general manner by the logarithmic function (4) of Book I, p. 79. It is apparent from the nature of this function that if it were possible to reduce the concentration of any of

the ions figuring in the equation to zero, an infinitely great change of electrode potential should take place. Actually we know that the titrate ions are never removed completely, but that they retain a finite though small concentration at and beyond the end-point of the titration. In order to emphasize this and the further fact that the end-point is the point at which the titrant added is exactly equivalent to the titrate originally present, we propose, following a practice introduced by Kolthoff and Furman, usually to refer to it as the " equivalence point ". The electrode reactions which determine the potential of an indicator electrode are frequently designated the " partial reactions " of the titration process.

We may represent a potentiometric titration by a curve in which mols titrant added per unit volume titrate are abscissæ, and the potentials of the indicator electrode are ordinates, changes in volume of the titrate being neglected. This curve should always be considered as extended beyond the equivalence point, and theoretically we obtain a close approximation to it, if we divide it into two distinct curves, the " pre-equivalence " and the " post-equivalence " branch. In the former we make the approximately correct assumption that the titrant is completely used up by the chemical reaction, and that its concentration is therefore zero, whereas in the latter the concentration of the titrate molecules is in the first instance assumed to be zero. In the pre-equivalence branch, as follows from what has already been explained, the ordinates approach infinity as the concentration of the titrate molecules approaches zero, the curve becoming steeper and steeper as the equivalence point is reached. The post-equivalence branch is determined by the concentration of the titrant molecules in a manner similar to that in which the titrate molecules determine the pre-equivalence branch, the concentration of the titrate ions being found when required by calculation from the (assumed) value of the titrant ions. As a result both branches are asymptotic to a straight line drawn perpendicularly to the axis of the abscissæ through the equivalence point, one approaching this line at plus, the other at minus infinity, and one is concave, the other convex, seen from arbitrarily chosen

points. Illustrations of titration curves are given below. The merging of a pre-equivalence into a post-equivalence branch is shown in fig. 1, B. The accurate positions of points on the composite curve are calculated by dropping the assumption of zero concentrations for any type of molecule, and estimating all concentrations by means of the law of mass action and of the constancy of total mass applied to each atomic species. Such calculations are considered below (pp. 18 *seq*.).
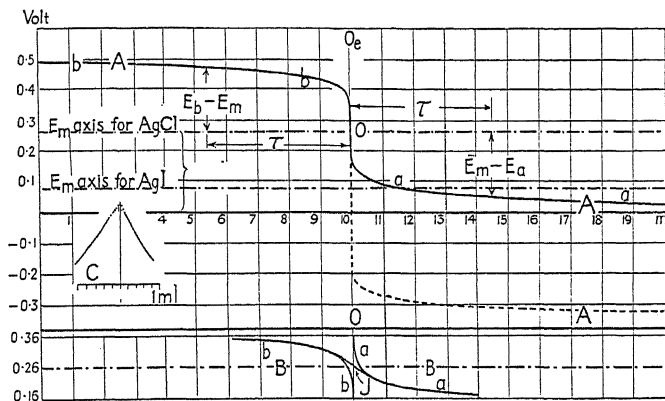
Fig. 1.—Illustrations of Titration Curves

Though simple in principle, mathematically they are involved. We shall start from the consideration of a simple instance, viz. the pre- and post-equivalence curves in the titration of a silver nitrate solution with chloride, a piece of silver serving as the indicator electrode. We shall also calculate the concentration of silver ions, and hence the electrode potential at the equivalence point. Thus we obtain the correct position of the composite curve at the equivalence point in place of plus and minus infinity shown by pre- and post-equivalence curves, and we shall be able better to understand how the latter two curves merge into each other.

The Titration of Silver by Chloride Ion.

The reaction is governed by the ionic equation $Ag^+ + Cl^- = AgCl$, and if the temperature is taken to be 17° C., the electrode potential is given by the equation

$$E = E_0 + 0\cdot058 \log [Ag^+], \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

in which the symbols have the same significance as in Vol. I (equation (6a), p. 80). Indicating the original molecular concentration of the titrate silver by C, the number of mols of titrant added per unit volume of titrate by t, we have, making the approximations discussed above, and assuming complete ionization, a pre-equivalence curve or branch, to which we shall refer by means of a b (before), and a post-equivalence branch, to which we shall refer by means of an a (after). For pre-equivalence

$$[Ag^+] = C - t, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1b)$$

and for post-equivalence

$$[Cl^-] = t - C. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1a)$$

It will have been understood that t is derived from the volume v_n of titrant added, its molecular concentration C_n, and the volume v_e of titrate by the relation

$$t = C_n \frac{v_n}{v_e}.$$

Since v_e is not constant but is the original volume of the titrate plus the volume of titrant added, t is not simply proportional to v_n. In all subsequent considerations we shall, however, neglect this, and consider t to be proportional to and hence a measure of the volume v_n of titrant added.

Indicating the solubility product of silver chloride by K_s, we have

$$[Ag^+][Cl^-] = K_s; \quad ((4a), \text{ Vol. I, p. 27})$$

hence for post-equivalence

$$[Ag^+] = \frac{K_s}{t - C}, \quad\quad\quad (2)$$

for which we also use the definition given in equation (5), Vol. I, p. 28,

$$-\log K_s = p_s. \qquad \ldots \quad \ldots \quad (2a)$$

Thus we have, by (1) and (1b), before equivalence,

$$E_b = E_0 + 0{\cdot}058 \log (C - t), \qquad \ldots \quad (3b)$$

and after equivalence, by (1), (2) and (2a),

$$E_a = E_0 - 0{\cdot}058 p_s - 0{\cdot}058 \log (t - C). \qquad (3a)$$

We deduce the following relations between values E_b and E_a of any two points on the b and a curves, for which

$$(C - t)_b = (t - C)_a = \tau,$$

i.e. we compare a point at which τ units titrant still have to be added to reach the end-point with one at which τ units in excess have been run into the titrate. Substituting τ into equations (3b) and (3a) respectively, and adding, we find

$$E_b + E_a = 2E_0 - 0{\cdot}058 p_s.$$

For the same pair of points we also calculate the distances $E_b - E_m$ and $E_a - E_m$ from a horizontal line or axis representing an electrode potential E_m half-way between E_b and E_a, i.e. a line for which

$$E = E_m = \tfrac{1}{2}(E_b + E_a) = E_0 - 0{\cdot}029 p_s. \quad . \quad (4)$$

We thus obtain

$$E_b - E_m = 0{\cdot}029 p_s + 0{\cdot}058 \log \tau \quad . \quad . \quad (4b)$$

and

$$E_a - E_m = -0{\cdot}029 p_s - 0{\cdot}058 \log \tau. \quad . \quad (4a)$$

Thus the pre- and post-equivalence curves have equal and opposite values for $E - E_m$ at equal distances τ from the end-point of the titration, and the composite titration curve has in this case a symmetry shown by curve A in fig. 1 (p. 3). This symmetry is of such a kind that the post-equivalence is evolved from the pre-equivalence curve by rotation through

180° around an axis passing perpendicularly to the plane of the paper through the point on the E_m axis for which $\tau = 0$. This point, which is the equivalence point on the E_m axis, we shall designate as O. The actual concentration $[Ag^+]_e$ at the equivalence point is not zero, as is assumed in equation (1*b*), but can be easily calculated when we remember that at the equivalence point not only is the chlorine combined with silver in the precipitated silver chloride equivalent to the silver, but also the small concentration of chloride ions left in solution is equal to that of the silver ions, or $[Cl^-]_e = [Ag^+]_e$. Substituting into equation (4*a*), p. 27, Vol. I, we find $[Ag^+]_e = \sqrt{K_s}$. We also calculate the concentration of silver ions which corresponds to the half-way potential E_m by substituting the value of E given in equation (4) into equation (1). Using also the definitions of p_s and K_s quoted above from Vol. I we here too obtain the result $[Ag^+] = [Cl^-] = \sqrt{K_s}$.

In fig. 1, B, a detailed representation of the course of the curves *b* and *a* corresponding to equations (3*b*) and (3*a*) near the equivalence point on the E_m axis is given, as well as that of a junction piece J which is derived by rigid calculation as explained above. In order to make the figure practicable, it has been necessary to magnify the abscissæ of the ordinary titration curve A a hundredfold, whereas the scale of the ordinates has remained unchanged. As a result what appears in figure A as an almost vertical line has been flattened out in B to a line covering four divisions of the abscissæ. It will be seen that the junction piece passes through the point O merging the opposite curvatures of the *b* and *a* branches in an inflexion point and becoming indistinguishable from the pre- and post-equivalence branches at a very short distance from equivalence. Thus calculation shows that for one division of the B diagram (10^{-4} molar) the difference between E and E_m calculated respectively by the approximate and by the accurate methods amounts to only 0·4 per cent (about 2×10^{-4} volt), and progressively becomes smaller with increasing concentration. It is due to the symmetry of pre- and post-equivalence curves in the case of the silver-chloride titration that inflexion and equivalence points occupy the

same position. Such symmetry is, however, by no means general for all titration curves, though opposite curvature is exhibited by pre- and post-equivalence branches. We shall thus in general have an inflexion point near the equivalence point, although its mathematical identity with the latter is not universal. Calculations made by Kolthoff and Furman have shown that the "titration error" made by assuming equivalence and inflexion points to be identical leads in most cases to only small errors.

In the example of a titration curve shown in fig. 1, A, the original concentration of the titrate silver is taken as tenth normal, i.e. $C = 0.1$, and the addition of each ml. titrant is assumed to reduce this concentration by one-hundredth normal. Thus, neglecting as above changes in concentration brought about by the addition of the titrant, the curve may represent the precipitation of, say, 100 ml. N/10 $AgNO_3$ by 10 ml. N/1 NaCl. As reference electrode a saturated calomel electrode has been taken, which may be supposed to have been connected to the titrate by means of an ammonium nitrate bridge. We may then take $E_0 = 0.55$ volt and $p_s = 10$. At the beginning of the titration ($C = 0.1$, $t = 0$) we have, by equation (3b), $E_b = 0.492$ volt. Similarly at a position 1/10 ml. before the end-point ($C - t = 0.001$) $E_b = 0.376$ volt, and 1/10 ml. after the end-point, by equation (3a), $E_a = 0.144$ volt. We thus see that whereas the change in potential from the beginning of the titration to 1/10 ml. from the end-point is 0.116 volt, the change from 1/10 ml. before to 1/10 ml. after the end-point is 0.232 volt.

Detection of the End-point of a Potentiometric Titration.

From the example just discussed in detail we recognize that we may detect the end-point of a potentiometric titration by the large change or "jump" in potential that is found there.

We obtain a much more accurate result by another method in which we plot changes of potential per drop of titrant against burette readings shortly before and shortly after equivalence. Starting, say, about 0.5 ml. before the end-point

we plot average change of potential in arbitrary units per drop of titrant added at, say, each tenth ml. of the burette reading against this reading. We thus obtain curves such as those shown (drawn-out lines) in fig. 1, C. We extrapolate these curves to their point of intersection (dotted lines), and take the latter to represent the end-point of the titration. It will be clear that we are thus plotting values of $\frac{dE}{dt}$ against t, and in this way obtaining the position of the maximum of $\frac{dE}{dt}$, or in other words the inflexion point. This method represents the most generally useful one available. Usually it is simplified by determining the position of the maximum change of potential per drop of titrant without the aid of a graph.

Thirdly, it is clear that the end-point of a titration may be detected, if its electrode potential is known. Details of the application of this principle will be discussed in Chapter II.

In conclusion we make reference to the calculation of the equivalence point from the position of points close to it, described in papers by Cavanagh, *J. Chem. Soc.*, 1928, pp. 843 and 855.

Comparison of the Titration of Silver by Chloride and by Iodide Ion. The Joint Estimation of different Ions.

From equation (3b) it is clear that the pre-equivalence branch of the titration curve is not affected by the salt precipitated. However, according to equation (3a) the post-equivalence values E_a differ according to the value of the solubility exponent p_s. Thus for silver chloride $p_s = 10$, for silver iodide $p_s = 16$, and by utilizing equation (3a) we find for post-equivalence $E_{AgI} - E_{AgCl} = -0.348$ volt. All potential values on the AgI post-equivalence curve are thus more negative than the corresponding ones on the AgCl curve by 0.348 volt as is shown by the broken part of curve A in fig. 1. As follows from equation (4), the potential E_m at the equivalence point is more negative by half this amount, viz. by 0.173 volt. It will thus be seen that the jump in potential near the equivalence point is much more marked, and that

the latter can be more accurately determined for iodide ion, used as titrant, than for chloride ion.

The principles discussed may be employed to estimate several ions present in the same solution in a single titration. Thus let us imagine that we have iodide and chloride present first separately, and secondly in the same solution, and let them be titrated potentiometrically by silver ion. In the former case we shall obtain titration curves which can be made identical with those shown in fig. 1, if instead of starting at the left of the diagram and proceeding to the right, we start at the right and proceed to the left. If on the other hand we titrate a solution containing both iodide and chloride ion with a silver solution, at first only the more insoluble silver iodide is precipitated, and the electrode potential is that shown by the iodide curve. It is only when the iodide ion has almost disappeared from solution that the concentration of silver ion rises sufficiently to allow also silver chloride to precipitate. The concentration of both iodide and chloride ion is then governed by the equations

$$[Ag^+][I^-] = K_{AgI} \quad . \quad . \quad . \quad . \quad (5b)$$

and

$$[Ag^+][Cl^-] = K_{AgCl}, \quad . \quad . \quad . \quad . \quad (5a)$$

from which

$$[I^-] : [Cl^-] = K_{AgI} : K_{AgCl} = 10^{-16} : 10^{-10} = 10^{-6}. \quad (6)$$

It thus appears that when silver iodide and chloride precipitates are both present, the concentration of the iodide ion is always one-millionth of that of the chloride ion. After silver chloride precipitate has been formed, the electrode potential may be read from the chloride curve. Chloride and iodide curves thus intersect at a point where the chloride concentration shows its original value, and the iodide concentration is one-millionth of this, i.e. practically zero. Fig. 2 shows the composite titration curve of 100 ml. solution containing one-millimol iodide and one-millimol chloride, by 25 ml. N/10 AgNO₃. Such a titration can be readily carried out. If, however, we had similar solutions of bromide and chloride,

the silver chloride would have begun to precipitate, when the concentration of the bromide followed from the ratio $[Br^-] : [Cl^-] = K_{AgBr} : K_{AgCl} = 5 \times 10^{-13} : 10^{-10} = 0.005$, and only an approximate determination would have been possible. Iodide and bromide may, however, be determined together
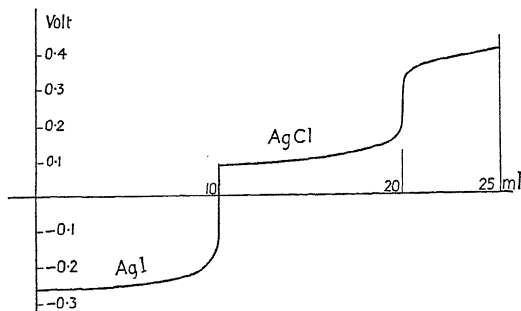
Fig. 2.—Composite Precipitation Curve

with appreciable accuracy, for here we have under similar conditions to those just contemplated a ratio of concentrations of 0.0002.

Neutralization of a Strong Acid by a Strong Base and vice versa.

It will be clear that the method described for the titration of silver by halide ion is applicable in principle to a large number of precipitation reactions. Further, it is identical, so far as form of titration curve is concerned, with the neutralization of a strong acid by a strong base, as represented by the equation $H^+ + OH^- = H_2O$ (Vol. I, p. 7, equation ($C3$)). Supposing a hydrogen electrode to be used as the indicator, and a saturated calomel electrode as the reference electrode, the titration equation and curve are identical in form with those representing a precipitation reaction. In this case, however, the value to be substituted for E_0 is the normal hydrogen potential $E = -0.25$ volt. Hydrogen and hydroxyl ion concentration have a constant product $K_w = 10^{-14}$, so

that for p_s we substitute $p_w = 14$. The equivalence point is calculated from equation (4) to show an indicator electrode potential of -0.66 volt. From what has been said and from equations (3b) and (3a) it follows that the pre-equivalence curve is represented by the equation

$$E_b = -0.25 + 0.058 \log(C - t) \text{ volt}, \quad . \quad . \quad (7b)$$

and the post-equivalence curve by

$$E_a = -1.062 - 0.058 \log(t \cdot C) \text{ volt}. \qquad (7a)$$

Neutralization of a Feeble Acid by a Strong Base, and of a Feeble Base by a Strong Acid.

The course of the neutralization of a feeble acid by a strong base has been discussed in Vol. I, pp. 44 *seq.* The reversibility of this reaction as exemplified by the hydrolysis of the salt formed was considered on pp. 31 *seq.* It was shown that on completion of neutralization the solution has an alkaline reaction, the p_H being given by equation (14) of p. 35. Thus if the acid is acetic acid, and the concentration of the titrate N/100, the p_H at the equivalence point is calculated to be 8·4, corresponding to a hydroxyl ion concentration of about 2.5×10^{-6} normal.

The general properties of the pre-equivalence curve may be derived from what was said on pp. 45 *seq.* regarding the course of p_H during the neutralization of a weak acid. Since changes in electrode potential are proportional to the negative values of p_H according to the equation

$$E = E_0 - 0.058 p_H, \quad . \quad . \quad . \quad . \quad (8)$$

the general character of the E curve is the same as that of the p_H curve, e.g. the electrometric titration curve shows an inflexion point at half neutralization corresponding to a minimum of dE/dt, concave passing into convex curvature or vice versa.

Corresponding to our previous practice, we indicate the original concentration of the titrate acid by C, and the mols titrant added per unit volume titrate by t. We assume the

original concentration of the salt formed to be zero; we also assume it be completely ionized, and the free acid to be practically undissociated. We then have

$$t = [A^-], \quad C - t = [HA]; \quad . \quad (9a) \text{ and } (9b)$$

also, by the law of mass action, applied to the equilibrium $HA \rightleftharpoons H^+ + A^-$

$$K_a = [H^+] \frac{[A^-]}{[HA]}. \quad . \quad . \quad . \quad . \quad (10)$$

Utilizing the relation $p_H = -\log[H^+]$ and eliminating $[H^+]$, $[A^-]$, and $[HA]$ from equations (8), (9a), (9b), and (10), we find

$$E = E_0 + 0 \cdot 058 \log K_a - 0 \cdot 058 \log \frac{t}{C - t}. \quad . \quad (11)$$

Considerations regarding the neutralization of a feeble base by a strong acid become identical with those regarding the neutralization of a feeble acid by a strong base, if H^+ is exchanged for OH^-, A^- for B^+, HA for BOH, and K_a for K_b.

The Determination of the Dissociation Constant of a Feeble Acid or a Feeble Base from its Titration Curve.

By means of equation (11), or the corresponding one for a feeble base, the titration curve of any feeble acid or base may be constructed if the dissociation constant K is known. Inversely, the equation furnishes a ready and very important means of determining K. For this purpose the value E_d of E at half (demi-) neutralization is determined experimentally. As follows from equation (11), by substituting $t = \frac{1}{2}C$, K may then be calculated for ordinary temperature from the relation

$$\log K = \frac{1}{0 \cdot 058} (E_d - E_0),$$

or, if the reference electrode is a hydrogen electrode, from $\log K = E_d/0 \cdot 058$.

The Titration of Two Feeble Acids present in the same Solution.

It follows from equation (11) that the titration curve of any one weak univalent acid at ordinary temperature differs from that of another only in the value of $0 \cdot 058 \log K$. This fact is of importance in the titration of two weak acids present in the same solution. In order to study such a titration more fully, we consider the acids I and II, having respectively the dissociation constants K_1 and K_2. We introduce the quantities n_1 and n_2, each defined as the " neutralization stage " by the equation $[A^-]/[HA] = n$, so that we have, by equation (10), $K_1 = [H^+]n_1$ and $K_2 = [H^+]n_2$. From these relations we find by division that for any given value of $[H^+]$

$$n_1 : n_2 = K_1 : K_2, \qquad (12)$$

or otherwise expressed, at any point during the titration the ratio of the neutralization stages of two weak univalent acids is the same as that of their dissociation constants. If, for example, the dissociation constant of the first is 10^4 times as great as that of the second, the titration of the acids takes place consecutively in as much as the neutralization stage of the first is throughout ten thousand times as great as that of the second, and a composite titration curve is obtained, having two branches which merge into each other in an inflexion point. According to Kolthoff and Furman an inflexion point between the titration branches of two feeble acids of equal concentration is recognizable only if the ratio of their K values is greater than 100. Similarly the practical limit for the titration of a weak acid by NaOH in tenth normal solution is reached when $K = 10^{-8}$.

The Neutralization of an Acid of Moderate Strength by a Strong Base.

In the mathematical equations representing the neutralization of an acid of moderate strength by a strong base, the concentration of the hydrogen ions is no longer negligible compared with that of the other molecular species. We thus

have to consider the two independent chemical equations which we shall indicate by a and b:

$$HA + OH^- = H_2O + A^- \quad . \quad . \quad . \quad . \quad (a)$$

and
$$H^+ + A^- = HA. \quad . \quad . \quad . \quad . \quad (b)$$
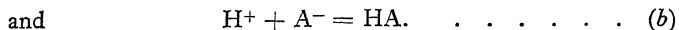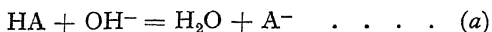
We indicate original concentrations by the subscript 0; thus the original concentration of the undissociated HA molecules is represented by $[HA]_0$. Where additions to the concentration of the titrate are made, we indicate these by the chemical symbol of the molecular species, and where separate increases are the result of the two chemical processes, a and b, we distinguish them by subscripts; thus HA_a and HA_b represent the algebraic increases in the concentration of HA resulting from the chemical processes a and b respectively. The concentration of OH^- ions we consider negligible. We thus have $[OH^-]_0 = 0$, and $[OH^-] = 0$ in place of the equilibrium equations resulting from the chemical equation a. The (partial) increase of the OH^- concentration of the titrate due to added titrant we indicate as previously by t, and the increase of the H^+ concentration by x. We then have, firstly, the equations representing total concentrations in terms of their components, viz. $0 = [OH^-] = 0 + OH_a^- + t$; $[H^+] = [H^+]_0 + x$; $[A^-] = [A^-]_0 + A_a^- + A_b^-$; $[HA] = [HA]_0 + HA_a + HA_b$. Secondly, we have the stoichiometric relations following from the chemical equations a and b, viz. $HA = OH_a^- = -A_a^-$ and $x = A_b^- = -HA_b$. Finally, we have the equilibrium equations between H^+, A^-, and HA for original, and for variable concentrations. From the system of equations thus obtained we can eliminate all the variables except t and x, and thus we obtain, after some calculation, the equation

$$([H]_0 + x)([A^-]_0 + t + x) = K_a([HA]_0 - t - x),$$

which may be employed to obtain values for the hydrogen ion concentration corresponding to various values of t.

In fig. 3 is shown the composite neutralization curve by NaOH of a solution containing a moderately strong univalent

acid having the dissociation constant 10^{-3}, and a weak acid
of dissociation constant 10^{-7}. The figure corresponds to a
concentration of N/100 for each acid, and to the neutraliza-
tion of one-tenth of each by 1 ml. titrant, e.g. to a volume of
100 ml., and to a tenth normal concentration of titrant. A
saturated calomel electrode was assumed to be the reference
electrode.
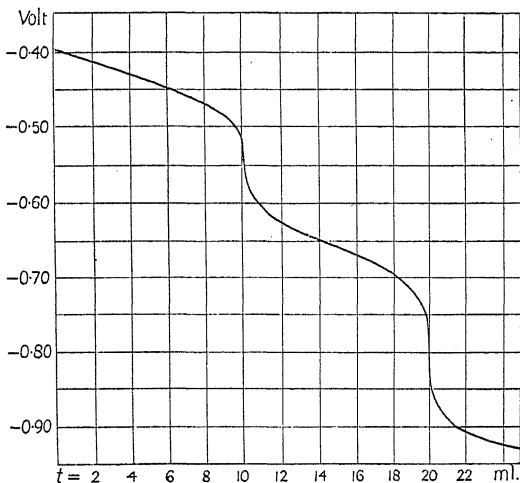
Fig. 3.—Composite Neutralization Curve

When a polybasic acid is titrated, the separate stages of
neutralization can often be recognized by separate inflexion
points. Thus in the titration of phosphoric acid the neutrali-
zation of the first hydrogen atom corresponds to that of a
moderately strong acid of dissociation constant $1 \cdot 1 \times 10^{-2}$,
that of the second to a weak acid of dissociation constant
$1 \cdot 95 \times 10^{-7}$. The neutralization of the third hydrogen atom
cannot be detected by an inflexion point, the corresponding
dissociation constant being given as $3 \cdot 6 \times 10^{-13}$.

Titration of a Reductant by an Oxidant and vice versa.

As an example we consider a titration based on the reaction

$$Sn^{++} + 2Fe^{+++} = Sn^{++++} + 2Fe^{++}.$$
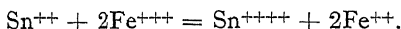
To simplify matters we assume the original concentration of stannic and ferrous ions to be zero. We indicate the original concentration in mols per unit volume, of the titrate stannous tin by C, and the mols of titrant ferric iron added per unit volume of titrate by t. Assuming as before complete reaction and complete ionization, and ignoring changes of volume during the titration, we have for pre-equivalence

$$[Sn^{++}] = (C - \tfrac{1}{2}t); \ldots \text{ and } [Sn^{++++}] = \tfrac{1}{2}t, \ldots (13b) \text{ and } (13b')$$

and for post-equivalence

$$[Fe^{++}] = 2C; \ldots \text{ and } [Fe^{+++}] = t - 2C. \ldots (13a) \text{ and } (13a').$$

The pre-equivalence curve for ordinary temperature is derived from the equation $(6f)$ (Vol. I, p. 80),

$$E = (E_0)_{Sn} + 0.029 \log \frac{[Sn^{++++}]}{[Sn^{++}]}; \quad . \quad . \quad (14b)$$

the post-equivalence curve from (*ibid.* equation $(6e)$)

$$E = (E_0)_{Fe} + 0.058 \log \frac{[Fe^{+++}]}{[Fe^{++}]}. \quad . \quad . \quad (14a)$$

Eliminating the variable concentrations of Sn and Fe by means of the four equations (13), we obtain for the pre-equivalence curve

$$E = (E_0)_{Sn} + 0.029 \log \frac{t}{2C - t}, \qquad (15b)$$

and for the post-equivalence curve

$$E = (E_0)_{Fe} + 0.058 \log \frac{t - 2C}{2C}. \quad . \quad . \quad (15a)$$

It will be seen that equation (15b) is analogous to equation (11). We shall therefore have for the oxidation of stannous ion a pre-equivalence curve of similar form to that representing the neutralization of a weak acid by a strong base, e.g. fig. 5a, p. 47, Vol. I. Thus there will be at half-equivalence, namely for $t = C$, an inflexion point corresponding to a minimum gradient of potential. Mathematically as in previous cases, the curves approach minus, plus infinity respectively, at the equivalence point, $(t = 2C)$. In actual fact, owing to the incompleteness of the chemical reaction, the curves merge into each other in an inflexion point corresponding to a maximum grade of potential. This point is taken as the end-point of the titration. It is close to the equivalence point, the electrode potential of which is discussed in the following section.

In some titrations chemical equilibrium is established fairly rapidly. This is the case in the pre-equivalence curve considered, and therefore experimental and calculated potentials may be expected to agree fairly closely. In other cases, the experimental curve does not correspond strictly to well-defined potentials arising from a reversible process. For example, in the titration of ferrous by dichromate ion, the post-equivalence potentials of a piece of platinum dipping into the titrate are the result of the electrode reaction

$$2Cr^{+++} + 7H_2O + 6F \rightleftharpoons Cr_2O_7^{--} + 14H^+,$$
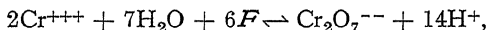
and are therefore governed theoretically by the equation

$$E = E_0 + \frac{0 \cdot 058}{6} \log \frac{[Cr_2O_7^{--}][H^+]^{14}}{[Cr^{+++}]^2}.$$

Actually only an approximation to this result may be expected. However, the equation shows that the electrode potential is the more positive the higher the hydrogen ion concentration, a tenfold increase of the latter making the potential more positive by 0·135 volt, and this is found to be qualitatively in accord with experiment. To obtain a high post-equivalence potential, and hence a large jump at the end-point, the solution must be made as acid as possible, the equivalence point

being taken as the highest point on the jump. Similar considerations hold for permanganate titrations.

The Determination of several Reductants or Oxidants in the same Solution.

When several reductants are oxidized in the same solution the more powerful reductant undergoes oxidation in preference to the feebler one in a manner determined by an equilibrium equation such as (12) (p. 89 of Vol. I). If the E_0 values of the two reductants differ sufficiently, say by 0·3 volt, their titration branches will be clearly distinguishable, and a composite titration curve is obtained of a character analogous to that represented in fig. 3 (p. 15). As explained in connexion with this figure, the completion of each reaction is recognized by the inflexion point through which the branch representing one reaction merges into the next branch. This principle has been employed for the simultaneous determination of iron and vanadium, and in other cases.

General Expression for the Equivalence and the Inflexion Point, and Formulation of the Titration Error.

We now come to the formulation in a few instances of expressions for the titration curve as a whole, and discard the differentiation between pre- and post-equivalent curves as distinct entities. Such calculations will comprise the determination of the equivalence and the inflexion point. We therefore drop the approximations expressed, e.g. by the equations (1b) and (1a) (p. 4), and confine ourselves to the following general principles: (1) Electrode potentials are expressed by the equations hitherto employed. (2) The increase or decrease in concentration of each molecular or ionic species which participates in the chemical reactions governing the titration follows from the equations of the latter, allowance being made for added titrant, and for loss due to precipitate removed from the solution. Where several independent chemical equations express the titration as in the example of the neutralization of an acid of moderate strength

given on p. 14, total changes may be treated as the sum of part changes, each of which is subject to the stoichiometric relations following from the chemical equations. (3) All concentrations are subject to the law of mass action.

(a) *Precipitation Reactions.*—We consider the precipitation of a salt as represented by the chemical equation

$$b\text{B}^+ + a\text{A}^- = \text{B}_b\text{A}_a,$$
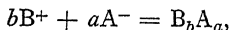
in which B^+ represents an a-valent basic ion, that is being titrated by the b-valent acidic ion A^-. We assume that the potential of a metallic indicator electrode is undergoing measurement, which is in electrical equilibrium with the B^+ ions. As before, we indicate the original concentration of the titrate B^+ ions (in mols per unit volume) by C, the mols of titrant added per unit volume titrate by t, and we neglect changes of volume in the titrate. The number of mols of precipitate B_bA_a formed per unit volume titrate we indicate by p. Theoretically there is a difference as to whether the salt B_bA_a is present as a precipitate at the beginning of the titration or not. In the former case the ion A^- has an initial concentration, which follows from its solubility product, but which is always negligible, whereas in the latter case the initial concentration of A^- is zero. We shall assume the latter case. We then have at ordinary temperature, by principle 1,

$$E = E_0 + 1/a \times 0\!\cdot\!058 \log [\text{B}^+]; \qquad (16)$$

by principle 2 we have

$$[\text{B}^+] = C - bp \qquad \ldots \ldots \quad (17)$$

and $\qquad\qquad [\text{A}^-] = t - ap; \qquad \ldots \ldots \quad (18)$

and, by principle 3,

$$[\text{B}^+]^b [\text{A}^-]^a = K_s. \qquad \ldots \ldots \quad (19)$$

We now proceed to calculate the value $[\text{B}^+]_e$ of $[\text{B}^+]$ at the equivalence point, i.e. the point for which

$$t : C = a : b. \qquad\qquad (20e)$$

Eliminating the variables p, $[A^-]$, and t from equations (17), (18), (19), and (20e) and transposing, we find

$$[B^+]_e = \left(\frac{a}{b}\right)^{\frac{a}{a+b}} K_s^{\frac{1}{a+b}}. \quad . \quad . \quad . \quad (21e)$$

We also calculate the value $[B^+]_i$ of the concentration $[B^+]$ at the inflexion point, i.e. we assume the relation

$$\frac{d^2E}{dt^2} = 0. \quad (20i)$$

From equations (17), (18), and (19) we eliminate the variables p and $[A^-]$, thus obtaining an expression for t in terms of $[B^+]$. By means of this and equations (16) and (20i), the following expression for $[B^+]_i$ has been found,

$$[B^+]_i = \left(\frac{b}{a}\right)^{\frac{3a}{a+b}} K_s^{\frac{1}{a+b}}. \quad . \quad . \quad . \quad (21i)$$

On comparing equations (21e) and (21i), it will be seen that inflexion and equivalence points are identical only when $a = b$. Let t_e and t_i indicate the values of t at these two points respectively. We then define the " titration error " ϵ by the equation

$$\epsilon = \frac{t_i - t_e}{t_e}. \quad . \quad . \quad . \quad . \quad (22)$$

By means of this equation, and utilizing also equation (20e) for the purpose of calculating t_e, and equations (17), (18), (19), and (21i) for the purpose of calculating t_i in terms of the given constants only, we find

$$\epsilon = \frac{1}{C} K_s^{\frac{1}{a+b}} \left[\left(\frac{b}{a}\right)^{\frac{a-2b}{a+b}} - \left(\frac{b}{a}\right)^{\frac{3a}{a+b}}\right]. \quad . \quad . \quad (23)$$

As an example of the employment of this equation, we may take the titration of Ag^+ by CrO_4^{--} in tenth molar solution. Making $C = 0.1$, $K_s = 2 \times 10^{-12}$, $b = 2$, $a = 1$, we find $\epsilon = -0.0015$. If the original concentration had been hundredth molar, the titration error would have been ten times

as great, i.e. a result based on the inflexion point would be about 1·5 per cent low. It is therefore desirable to base titrations of silver by a bivalent ion on the precipitation of salts with a smaller solubility product than that of silver chromate.

Example of the Calculation of the Electrode Potential at Equivalence in the case of an Oxidation-reduction Reaction.

We conclude this section by calculating the equivalence electrode potential at ordinary temperature in the titration of stannous tin by ferric iron according to the ionic equation given on p. 16. We assign to the symbols C and t the same meaning as given to them there. The original concentrations of the stannic and ferrous ions may have positive values. If these are equivalent, they do not affect the final result, if not, the result becomes unnecessarily involved. The original concentration of the ferric ions is always negligibly small, and may be calculated from the equilibrium equation. As on p. 16 we propose to assume all original concentrations except that of the stannous tin to be zero. For equivalence we have

$$t : C = 2 : 1. \tag{24}$$

By principle 1,

$$E = E_{0\text{Fe}} + 0·058 \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}$$

$$E_{0\text{Sn}} + 0·029 \log \frac{[\text{Sn}^{++++}]}{[\text{Sn}^{++}]}; \quad (25a) \text{ and } (25b)$$

by principle 2,

$$t - [\text{Fe}^{+++}] = 2(C - [\text{Sn}^{++}]), \quad . \quad . \quad . \tag{26}$$

$$C - [\text{Sn}^{++}] = [\text{Sn}^{++++}], \quad . \quad . \quad . \quad . \tag{27}$$

$$t - [\text{Fe}^{+++}] = [\text{Fe}^{++}]; \quad . \quad . \quad . \quad . \quad . \tag{28}$$

and by principle 3,

$$\frac{[\text{Sn}^{++++}][\text{Fe}^{++}]^2}{[\text{Sn}^{++}][\text{Fe}^{+++}]^2} = K. \quad . \quad . \quad . \tag{29}$$

From equations (24), (26), (27), (28), (29) we calculate for each of the concentrations, values from which t and all the other concentrations except C have been eliminated. These values we substitute in equations (25a) and (25b), and find for the equivalence potential E_e,

$$E_e = E_{0Fe} \cdot \frac{0 \cdot 058}{} \log K = E_{0Sn} + \frac{0 \cdot 058}{6} \log K, \quad (30a) \text{ and } (30b)$$

from which follows

$$E_{0Fe} \cdot E_{0Sn} = \frac{0 \cdot 058}{2} \log K. \quad . \quad . \quad . \quad (31)$$

This agrees with equation (13) given on p. 90 of Vol. I. Substituting $\log K$ from equation (31) in either (30a) or (30b), we find

$$E_e = \tfrac{1}{3} E_{0Fe} + \tfrac{2}{3} E_{0Sn},$$

and taking the values given for E_{0Fe} and E_{0Sn}, likewise on p. 90 of Vol. I, we find for the equivalence potential referred to the hydrogen electrode $E_e = 0 \cdot 33$ volt.

APPARATUS AND METHODS

Titrations with the Apparatus used for Gravimetric Electrolytic Analysis.

Most potentiometric titrations can be carried out with the apparatus which has been described in connexion with gravimetric electrolytic analysis.

Burettes.

When used with a stand fitted with a stirrer, and for the titration of hot liquids, the jet of the burette should end some inches away from vertical below the graduation. A suitable arm should therefore be fitted, or a burette with arm and vertical stopcock be employed. The burette may conveniently be fitted to the stock-bottle and be arranged for filling automatically to zero. Its height should be made adjustable. For small stock-bottles this can be done by holding the bottle in a clamp fitted to a heavy stand. For heavy bottles of several litres capacity the burette is fitted to a separate holder, which can be raised or lowered on an upright fastened to the bottle, and must be connected to the latter by a suitable length of rubber tubing. In this case the burette is filled by suction conveniently obtained from a fair-sized bicycle pump in which the usual position of steel guard washer and leather washer have been exchanged, after reversing the original direction of the latter. Near the bottom of the pump a hole is drilled, which is covered by the thumb while the pump is used, and is released for the admission of air.

Indicator and Reference Electrodes and the Electric Circuit.

The inner electrode described for use in gravimetric analysis (pp. 21 and 22 of Vol. II) forms a convenient combined stirrer and indicator electrode when connected to the stand in the usual way, and used in conjunction with its tripod, the legs of which serve as useful baffles. To prevent the tip of the auxiliary electrode from fouling the revolving electrode, a bar may be fitted between the tops of two adjacent legs. This may consist either of platinum wire or of thin glass rod sealed to the legs. The saturated calomel electrode can be employed as a reference electrode, the same vessel being employed as for gravimetric analysis. The same precautions are taken, and the chloride in the connecting solution is replaced by other electrolytes when necessary. The potential difference between the indicator and the reference electrode is read directly on the high resistance voltmeter (50,000 Ω) (*vide* Vol. II, p. 37, fig. 28). As a rule the use of a zero method is unnecessary. When the indicator electrode is a hydrogen electrode, the fluctuations in resistance produced by the gas bubbles, however, make the use of the potentiometer box (Vol. II, p. 38, fig. 29) necessary. This is also useful for occasional checks on the resistance of the reference electrode.

As it is not absolute values of potential differences that are required, but only their changes during titration, it is useful to balance out the initial P.D. between the indicator and the reference electrode by the method of Roberts (*J. Amer. Chem. Soc.*, 1919, **41**, 1358). This is explained by the diagram (fig. 1). A single accumulator B is placed across the ends of the rheostat R, which is provided with a central tapping P and a slider Sl. By moving the latter from one end of the rheostat to the other, the potential difference between P and Sl can thus be varied between one-half of the positive and one-half of the negative value of the E.M.F. of the battery B, and the initial P.D. of the combination under measurement can be balanced out. The slider is connected to the indicator electrode Ei, and the tapping P to one of the terminals of the

high-resistance voltmeter G, the other terminal being connected to the reference electrode Er. By comparison with fig. 22, Vol. II, p. 29, it is seen that the connexions required are readily obtained on the ordinary electrolytic stand. The terminal P is provided on the stand; the indicator electrode is pushed into the inner electrode clutch, and the reversing key RS set so as to connect this clutch to the slider. Both the main and the shunt switch are closed. The voltmeter having been set to zero at the beginning of the titration, and usually having a unidirectional scale, must be connected so that the
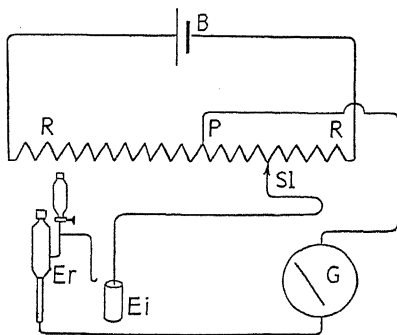
Fig. 1.—Balancing out initial P.D. between Electrodes

pointer moves across the scale during the progress of the titration. For oxidation titrations, neutralizations of alkali by acid, and precipitation reactions of negative ions, the indicator electrode is therefore connected to the positive, the reference electrode to the negative terminal of the voltmeter, whereas for reduction titrations, neutralization of acid by alkali, and precipitation reactions of positive ions, the reverse connexion is made.

The platinum electrode may be used directly for all oxidation or reduction titrations, including neutralizations of acids in the presence of quinhydrone. Where a silver or a mercury indicator electrode is required, the same electrode may be employed if it is plated with silver from a cyanide solution (Vol. II, p. 56), or with mercury at high-current density from an

acidified nitrate solution. It may also be used as an antimony electrode as discussed on p. 34 or as an electrode of the second order, i.e. as a silver halide or sulphide electrode, as described on pp. 36 *seq.*

The end-point of the titration, when using the apparatus discussed, is usually detected by determining the position of maximum change of potential per unit of titrant as explained on pp. 8 and 9. When potential change-drop titrant curves are employed, great accuracy can be obtained. The volume of a drop is determined from the number of drops in a millilitre or other suitable volume. In some cases it may be convenient to set the slider before beginning a titration at the potential of the end-point. This is then detected as described for the Pinkhof electrodes (p. 29).

Other Principles and Apparatus

Potentiometers, the Electron-beam Sectrometer, and the Valve-voltmeter.

Instead of the high-resistance voltmeter, potentiometers were employed in all the earlier work for measuring the P.D. between indicator and reference electrode, a capillary electrometer usually serving as a zero-instrument. The latter may occasionally be useful in connexion with the Pinkhof method of end-point detection described below. Another instrument which has been strongly recommended, particularly for use with bimetallic electrode systems (see p. 31), is the electron-beam sectrometer discussed on pp. 6 and 8 of Vol. II. In addition to the details given there, mention should be made of a switch provided to throw into the circuit a current suitable for polarizing a bimetallic system consisting of two originally identical platinum wires (p. 32).

Another modern development, first introduced by K. H. Goode (*J. Amer. Chem. Soc.*, 1922, **44**, 26), is the employment of the valve-voltmeter. Like the electron-beam sectrometer, this consumes only a negligible amount of current, and

therefore makes measurements almost independent of the resistance of the circuit. Considerable simplifications in the design and construction of other apparatus are thus rendered possible. Fig. 2 shows a circuit designed by Hiltner for purposes of potentiometric analysis (*Ausführung potentiometrischer Analysen*, and *Chem. Fabrik*, 1933, **6**, 111). This circuit may be considered to be a modification of circuits previously designed by G. T. Winch (*J. Inst. Elect. Eng.*, 1930, **68**, 533), and by Vickers, Sugden, and Bell (*Chem. and Ind.*,
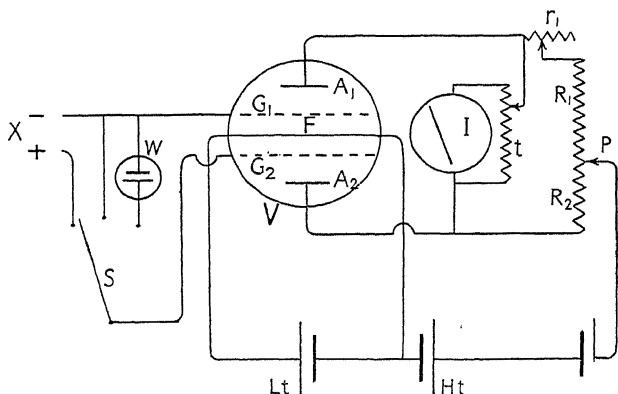
Fig. 2.—Circuit designed by Hiltner

1932, **51**, 545). Its characteristic feature is the employment of a double triode or "twin" valve V. The two halves of this valve are served by a common filament F, fed by the low-tension battery Lt. The three-way switch S allows the two grids G_1 and G_2 to be connected to the unknown potential difference X, or to be short-circuited, or to be applied to the poles of a standard cell W. The current from the anode battery Ht is branched at the point P, so that after passing respectively through the parallel resistances $R_1 + r_1$ and R_2, and the two anodes (plates) A_1 and A_2, it returns through the filament F. The P.D. between the ends of $R_1 + r_1$ and R_2 is measured by means of a suitable instrument I, the sensitivity of which

can be regulated by means of the shunt t. The resistances R_1 and R_2 are suitably obtained as the branches of a potentiometer of about 10,000 ohms, the adjustable rheostat r_1 having a resistance of about 500 ohms. The position of the point P thus gives coarse, and the position of the slider of r_1 fine adjustment of the two anode currents. The valve recommended by Hiltner is described as Valvo NZ/420. If the instrument I is suitably shunted, the unipivot voltmeter of 50,000 ohms resistance recommended for use in gravimetric analysis may be employed as I.

To adjust the valve-voltmeter before measurements, the switch S is first set so as to short-circuit the grids, and the anode currents are adjusted by means of P and the slider of r_1 to bring the pointer of the voltmeter to zero position. The switch is next set so as to interpose the standard Weston cell between the grids, and the voltmeter-shunt t is adjusted to bring the reading to 1·018 volts. It will then be found that on interposing unknown potential differences the voltmeter will give correct readings.

It will be noticed that the combination of grids gives floating potentials, the differences according to Hiltner being completely stable. In the circuit described by Vickers, Sugden, and Bell (see above), the double triode is replaced by two single carefully matched triode valves, No. H.L. 410, the filaments of which are fed in parallel from the same battery. They are operated at approximately zero grid bias, the unknown P.D. being interposed between the filament and the grid of the second valve. Direct adjustments of the anode currents are dispensed with, and instead, a potential divider fed from a small battery is employed for fine adjustment of the grid bias of the first valve at approximately zero value.

Perfect stability is claimed by their designers both for the double triode and for the matched triodes circuits. An advantage of the former circuit appears to lie in the fact that greater reliance may be placed on the two anodes being affected in an identical manner by extraneous interfering circumstances, and also that a grid-bias battery is dispensed with.

Reference Electrodes.

The Pinkhof Electrodes.

The proposal to use as a reference electrode one which shows the same potential as the indicator electrode at the end-point of the titration was made by Pinkhof in 1919 (*Dissertation*, Amsterdam). The end-point is then characterized by the deflection of the indicator instrument passing from a positive value through zero to a negative value, or vice versa. Obviously each kind of titration requires its own reference electrode, or "bottled end-point" as it has been called by Callan and Horrobin (*J. S. C. I.*, 1928, **47**, 329). The simplest bottled end-point is a solution of the same composition as the one undergoing measurement and having the same indicator electrode, titrated to its end-point (W. D. Treadwell and L. Weiss, *Helv. Chim. Acta*, 1919, **2**, 680). Numbers of other possibilities will suggest themselves. Thus a quinhydrone electrode placed in a suitable buffer solution may be used. Similarly silver or mercury electrodes in contact with accurately defined solutions of their soluble or sparingly soluble salts may be employed.

Electrolyte Bridges.

Bridge junctions to bring the reference electrode into electrical communication with the titrate electrolyte usually contain a strong solution of potassium chloride or of ammonium nitrate. In fig. 3, A represents a bridge fitted with end-plates of fritted Jena glass to prevent mixing of the solutions which have been connected. A simple bridge which can be readily prepared in the laboratory is that due to Erich Müller, which is shown in fig 3 at B. It is prepared from two T pieces, which are joined by a short rubber connexion c. The ends a_1 and a_2 are closed with stoppers of filter paper. To prepare these a small amount of dry filter paper is first pushed into the ends a_1 and a_2, and then small wads which have been soaked in the connecting solution are introduced through b_1 and b_2 and firmly tamped down with a

broad knitting needle to a total length of about $\frac{1}{2}$ cm. The connecting solution is introduced through one of the ends b by means of a capillary funnel until it reaches slightly above the level of c; b_1 and b_2 are then connected by means of a suitable piece of rubber tubing.

The type of bridge most frequently used is the agar gel bridge. To prepare this a suitable amount of the connecting solution, usually saturated KCl, is heated to its boiling-point. 3 per cent of its weight of agar powder is then introduced,
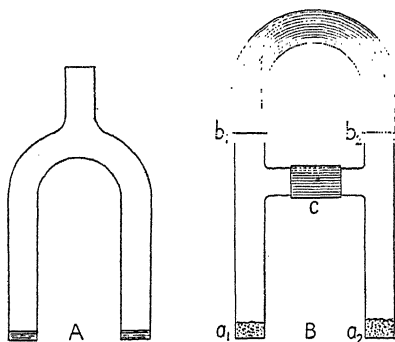
Fig. 3.—Erich Müller Bridge

and the solution is kept hot until the agar has completely dispersed. Suitable U-tubes are filled with this liquid by means of a pipette. After cooling, the tubes are topped up with more of the agar solution, and stored in a bottle containing connecting solution. Cords of viscose moistened with the electrolyte and placed in glass or rubber tubes may also be used.

Reference Electrodes for Use with the Valve-voltmeter.

For use with the valve-voltmeter Hiltner has described a number of reference electrodes. In place of mercury plus calomel a silver or silver-coated platinum wire which has been covered electrolytically with silver chloride is employed. This is housed in a glass tube, the lower part of which holds

a gelatinized potassium chloride or ammonium nitrate solution, whereas the closed upper part into which the wire dips contains a saturated potassium chloride solution. Instead of silver chloride plus KCl, silver iodide plus KI may be employed. Electrodes of this kind are placed in the titrate without any further connecting bridge.

Retarded Reference Electrodes: Differential Titration.

The retarded reference electrode is a second indicator electrode, which is placed in a solution in communication with the main titrate solution, but slightly lagging behind it in the amount of titrant it has received. A certain potential difference will exist between the two indicator electrodes. During the main part of the titration this will be immeasurably small, but near the equivalence point it becomes appreciable, and rises to a maximum at the inflexion point. Several methods for operating this principle exist. Cox (*J. Amer. Chem. Soc.*, 1925, **47**, 2138) divided the titrate into two equal parts which were placed in beakers connected by a bridge. The titrant was introduced from two burettes of which one lagged behind the other by a small fixed amount. The method is known as that of differential titration. Of other suggestions we mention only that due to Erich Müller (*Z. angew. Chem.*, 1928, **41**, 1152), in which the retarded indicator electrode is placed near the bottom of a capillary dipping into the titrate, and is thus removed slightly from immediate action by the titrant.

Bimetallic Electrode Systems.

The effectiveness of the so-called bimetallic electrode systems is based on a similar principle to that of the retarded electrodes. Bimetallic systems have been employed mainly in oxidation-reduction titrations. The indicator electrode is of platinum which comes to a true equilibrium potential with the titrate solution rapidly, whereas the reference electrode lags behind equilibrium to such an extent as to remain almost unaffected by the addition of titrant. As reference electrodes in bimetallic systems, palladium, silicon carbide,

and tungsten have been recommended. The last-named tends to become dull and inconstant when used continuously in oxidizing solutions. It may be restored by dipping the bimetallic system into fused sodium nitrite for 5 to 10 sec. at a temperature slightly above the melting-point of the latter (Smith and Sullivan, *J. S. C. I. (T.)*, 1937, **56**, 104).

Experiments have also been carried out in which two electrodes of the same metal subjected to different preliminary treatment have been employed. Thus smooth platinum and platinum covered with platinum black have been combined to form a bimetallic system. Willard and Fenwick (*J. Amer. Chem. Soc.*, 1922, **44**, 2516) use two identical platinum wires, one of which is polarized anodically, the other cathodically, during the titration by a current of about 50 microamps. Bimetallic systems have also been constructed for use in acid-alkali neutralizations. (For literature see N. Howell Furman, *Ind. Eng. Chem. Anal.*, 1930, **2**, 413.)

Indicator Electrodes

Gas Electrodes.

Gas electrodes were amongst the earliest to find technical application. The use of the hydrogen electrode in the titration of strong acids and bases was studied very completely by W. Böttger towards the end of the last century (*Z. physikal. Chem.*, 1897, **24**, 253). The method was considerably simplified by the writer in 1911, and papers were published by him in conjunction with J. T. Wood and D. J. Law (*J. S. C. I.*, 1911, **30**, 3 and 872) in which its application to the titration of tan liquors was described. Essentially the same apparatus was used by J. H. Hildebrand in 1913 in a very complete study of the potentiometric titration of acids and bases (*J. Amer. Chem. Soc.*, 1913, **35**, 847). The writer's apparatus is frequently ascribed to Hildebrand. The modified hydrogen electrode introduced by Hildebrand is described on p. 91, and is very commonly employed at the present day. The necessity to use a potentiometer in gas titrations has already

been referred to. The use of the hydrogen electrode is limited by the facts that certain substances such as cyanides, sulphites, &c., destroy or " poison " the catalytic efficiency of the platinum black, and that the electrode cannot be satisfactorily used in the presence of oxidizers, including the ions of all metals more noble than hydrogen. For instructions on platinizing the electrode, i.e. coating it with platinum black, see pp. 64 and 65.

In the presence of oxidizers the oxygen or the air electrode may be employed. In this the hydrogen is replaced by oxygen or air, the apparatus remaining otherwise unchanged (N. H. Furman, *J. Amer. Chem. Soc.*, 1922, **44**, 2685; J. Britton, *Trans. Faraday Soc.*, 1924, **20**, 740). Theoretically the use of the oxygen electrode is based on the equilibrium $2OH^- + 2F \rightleftharpoons O_2 + H_2O$. In practice, however, this equilibrium is not attained. If a small current is passed from a platinum electrode into an electrolyte solution, a positive overpotential is established which decays slowly. On the other hand, if a piece of platinized platinum in the same solution is surrounded by oxygen, its potential lags behind or remains negative to the true equilibrium value. Thus thermodynamical calculations based on high temperature gaseous equilibria show that the equilibrium potential between an oxygen and a hydrogen electrode placed in the same solution is 1·23 volts at atmospheric pressure. On the other hand, direct experiments with oxygen electrodes saturated with the gas under atmospheric pressure do not yield a greater value than about 1·1 volts. J. A. V. Butler and G. Armstrong (*Trans. Faraday Soc.*, 1933, **29**, 862) state that a close approach to the true equilibrium potential is attained when a bright platinum electrode is polarized anodically for about 10 sec., and this is followed by a small cathodic polarization produced by the momentary use of a reversing switch. According to Furman and to Britton (*loc. cit.*), the lag behind equilibrium potential does not prevent the use of the oxygen electrode in ordinary analytical determinations.

The Quinhydrone and the Oxide Electrodes.

Any electrode the potential of which depends on p_H may in principle be employed as an indicator in acid-alkali neutralizations. The most important is the quinhydrone electrode discussed in Vol. I, p. 94. To employ it a small amount of quinhydrone is added to the titrate. A platinum electrode of any form—for example, the inner electrode referred to on p. 24—may be used as the indicator electrode. Since quinhydrone is unstable in air at high p_H values, and moreover, being a weak acid, yields hydrogen ions to the titrate, it cannot be employed in alkaline solution. The highest p_H value at which it may be used is given as about 8, and in general the titration should be performed from acid to alkaline, and not in the reverse direction.

Metals in contact with their oxides or hydroxides, and mixtures of successive oxides, will show a potential dependent on p_H if they are capable of ionic interchange with the solution, according to the equation $MeO_n + H_2O = MeO_{n+1} + 2H^+ + 2\epsilon$. One of the most generally useful of the oxide electrodes is the antimony electrode which was discovered by Uhl and Kestranek in 1923 (*Monatsh*, 1923, **44**, 29). Its p_H range of usefulness is given as from 1 to 13. Metallic antimony ordinarily has a coating of oxide, which makes it suitable for use without further treatment. It may be employed in the form of a rod, or it may be deposited electrolytically on a platinum electrode. Hiltner (*Ausführung potentiometrischer Analysen*, p. 34) gives the following prescription:

A stout piece of platinum wire of about 1 cm. length which has been fused into a glass tube is plated with mercury from a chloride or nitrate solution with a current of 0·4 to 1 m.a. for a maximum of about 2 minutes. The wire is dried by gently heating, and is then plated from a 25 per cent solution of $SbCl_3$ in dry acetone by a current of about 1 m.a. until the antimony forms a dense continuous layer on the platinum. The electrode is washed first with dry acetone, and then for some minutes with dilute hot caustic soda. After that it is polarized anodically for a few minutes in dilute sulphuric acid, using a P.D. of about 4 volts between it and a platinum cathode.

Another element which provides a satisfactory indicator electrode in acid-alkali titrations is tungsten. This electrode was discovered by J. R. Baylis (*Ind. Eng. Chem.*, 1923, **15**, 852), who employed it in water analysis, using the filament of an ordinary incandescent electric lamp.

The Glass Electrode.

The glass electrode and its application are discussed in connexion with p_H measurements. When protected by a suitable shield, as suggested by Harrison (*J. C. S.*, 1930, 1538), it may be employed as an indicator electrode in potentiometric titrations, the methods of control being employed which are discussed in Section IV.

Metal—Metal Ion Electrodes.

It might be thought that a wide field for the titration of metal ions would be available by using as an indicator electrode the metal to be determined. Actually most of the baser metals in contact with solutions of their ions do not assume their correct potentials rapidly owing to the presence of films of oxide and adsorbed gas. The only metals that have found extensive application are silver and mercury. These are most commonly employed in the form of deposits on platinum as already mentioned. Dutoit and v. Weisse (*J. Chim. phys.*, 1911, **9**, 578) succeeded in extending the use of indicator electrodes to metals less noble than silver by depositing a very small amount on the indicator electrode during titration, and thus ensuring a permanently fresh and clean surface. Care was taken to keep the amount of metal thus removed from the solution negligible compared with the total amount present. This method appears to have found little favour. The substitution of silver chloride for silver electrodes is discussed below.

Indicator Electrodes of the Second Order.

An electrode of the second order is one in which a metal, say silver, is in equilibrium with the saturated solution of one of its sparingly soluble salts such as the chloride, conductivity

being imparted to the solution by the presence of another electrolyte having the same anion as the sparingly soluble salt. Thus the various calomel standard half-cells we have described, and the mercury cathode of a Weston cell, are electrodes of the second order. The use of electrodes of the second order in potentiometric analysis has been developed particularly by Hiltner (*Z. anal. Chem.*, 1933, **95**, 39), the most important examples being electrodes of silver used in conjunction with either the chloride, bromide, iodide, or sulphide of the metal, and also the corresponding electrodes of mercury. The silver salts may be produced electrolytically on the metal, which is conveniently deposited from a cyanide solution on the inner stirring electrode of gravimetric analysis with a current density of 1 to 5 m.a. per square centimetre. A coating of chloride, bromide, or iodide is then obtained by brief anodic treatment with a small current density in a solution containing the required anion. A coating of sulphide is similarly obtained from a dilute ammonium sulphide solution, the time of deposition being kept under five minutes, and the layer as thin as possible. The silver compounds mentioned all conduct the current, and the deposited layer of salt, if kept thin, does not prevent the electrode from functioning as a silver electrode. Similarly, when a platinum wire has been completely coated with silver halide by careful fusion of the latter, enough silver is present to allow the electrode to function as a silver-silver halide electrode for use with the valve-voltmeter.

As an example for the theoretical consideration of indicator electrodes of the second order, we take a silver-silver iodide electrode. If such an electrode is placed in a solution containing neither silver nor iodide ions, it will produce these in equal concentration, each being equal to $\sqrt{K_{\mathrm{AgI}}}$ or 10^{-8} mol per litre approximately, K_{AgI} being the solubility product of silver iodide. The potential of the electrode will be that shown at the equivalence point on the E.M. axis of the AgI curve of fig. 1, A (p. 3). A minute addition of free silver or iodide ion produces a large jump in potential. If the titrant or titrate contains silver or iodide ions, there is theoretically

no need for the addition of silver iodide, nevertheless there are cases in which a silver-silver iodide electrode functions better than a simple silver electrode, namely when oxidizers such as ferric salts, which passivate a silver indicator electrode, are present.

There are other cases, however, in which the silver-silver iodide electrode is an important detector for anions owing to the fact that it imposes an initial though minute silver ion concentration on the solution. Any titrant anion that is capable by combination with silver to form an insoluble compound or very stable complex that reduces the silver ion concentration still further, will be detected by a jump in potential. Thus if we impart an ionic concentration of 10^{-8}N of sulphide ion S^{--} to the titrate, Ag_2S, having an ionic product of about 10^{-50}, will be formed, and the concentration of the silver ions will be reduced from $\sqrt{K_{AgI}}$ to $\sqrt{K_{Ag_2S}/[S^{--}]}$, i.e. in the ratio of about 10^{-13}. A negative jump of about 0·75 volt is thus produced. Under such circumstances there is a tendency for the silver iodide of the indicator electrode to be converted into silver sulphide. This, however, has no effect on the result of the titration, and is of little practical importance. On the other hand, if we were using CN^- as the titrant with an AgI indicator electrode, the formation of the soluble complex $Ag(CN)_2^-$ would cause rapid solution and disappearance of the AgI electrode. In this case Ag_2S may be employed, since solution of this compound in cyanide is so slow as to be negligible (Hiltner, *Z. anal. Chem.*, 1933, **95**, 37).

It will be understood that it is not possible to employ AgI as an indicator electrode for a titrant ion forming a much more soluble silver salt than the iodide. Thus if Cl^- were the titrant and, say, Hg_2^{--} the titrate, the solubility product governing the titration would be that of AgCl, i.e. about 10^{-10}. To reduce the Ag^+ concentration below the original value of about 10^{-8} normal imposed by the iodide indicator electrode to 10^{-9} normal, and thus bring about a reduction of electrode potential of 0·058 volt, would require a Cl^- concentration of tenth normal in the titrate, whereas a reduction by another 0·058

volt would require a normal Cl⁻ concentration. On the other hand, if I⁻ were the titrant, and AgCl the indicator electrode, the original Ag^+ concentration would be about 10^{-5} normal, and an addition of free iodide ion to a concentration of 10^{-8} normal would reduce the silver ion concentration to 10^{-8} normal, causing a jump in potential of about 0·174 volt. Here there would be a tendency for the chloride indicator electrode to be covered by an iodide coating. This would, however, not interfere appreciably with the titration.

Indicator Electrodes for Oxidation-Reduction Equilibria.

For oxidation and reduction reactions a smooth platinum indicator electrode is always used. The inner stirring electrode of gravimetric analysis is quite suitable. Two distinct applications present themselves. First we have simple oxidation or reduction reactions in which the titrant acts in its capacity of an oxidizing or reducing agent. Distinct from this are the titrations in which the oxidant or reductant acts as a precipitating agent, its presence in excess being recognized by means of a simple platinum indicator electrode after some of the reduced (or respectively of the oxidized) form has been added to the titrate. Thus the reductant ferrocyanide ion may be used as a precipitant for zinc, the oxidant ferricyanide ion having been added previously either to titrant or titrate. Similarly, when iodide ion is used as a precipitant, its presence in excess may be recognized by a platinum indicator electrode, if the titrate has been saturated with iodine by the addition of a small amount of a freshly prepared alcoholic iodine solution.

INDIVIDUAL TITRATIONS

It might be thought that titrations can always be carried out potentiometrically when it is possible to formulate an electrode reaction on which the behaviour of an indicator electrode can be based. We have noticed, however, that owing to passivation and other causes indicator electrodes do not in all cases respond correctly to the concentrations of the ions with which they are assumed to be in equilibrium. It is thus necessary to test each reaction separately for its suitability for potentiometric titration. In the sequel we give a collection of some of the more important determinations that can be performed potentiometrically.

Acid and Alkali Determinations.

The potentiometric theory of neutralization has been discussed on pp. 10 to 15, and the practical methods available and their limitations on pp. 23 to 35.

Cations

Silver.—Titrants may be salts of one of the following ions: chloride, bromide, iodide, sulphocyanide. Bromide and iodide are said to give inaccurate results, owing to strong adsorption on their silver salts. The addition of about 1 gm. barium nitrate per 100 ml. solution is beneficial. Indicator electrode: silver or a suitable indicator electrode of the second order.

Gold.—The gold is first oxidized completely to the auric state by excess chlorine, and then titrated with either ferrous or stannous ions. The removal of the excess chlorine is shown by a first inflexion, which marks the beginning of the reduction

from the auric to the aurous state. The concentration of the hydrochloric acid in the solution must be kept small. Indicator electrode: platinum.

Mercury (mercuric).—Titrant: potassium iodide. The titration is carried out to the first inflexion point, i.e. to complete precipitation of HgI_2. Indicator electrode: silver iodide.

Mercury (mercurous).—The titrant may be one of the following: chloride, bromide, iodide, sulphocyanide. Indicator electrode: mercury deposited on platinum.

Copper (cupric).—Precipitation as sulphide by Na_2S solution. The titrate is buffered with about 30 ml. of a 2N acetate solution per 100 ml., and the titration performed rapidly to prevent adsorption of titrant on the precipitate. Indicator electrode: Ag_2S.

Copper (cuprous).—Precipitation as thiocyanate. To about 100 ml. solution are added 20 ml. 2N sodium acetate and enough hydrazine sulphate to decolourize completely. The solution is then acidified with dilute sulphuric acid, and an excess of N/10 standard thiocyanate having been added, it is titrated back with silver nitrate. Indicator electrode: Ag or AgI.

Bismuth.—The method recommended is to precipitate the bismuth completely as oxychloride by means of an excess of standard N/10 HCl from a hot solution after buffering with sodium acetate. After filtering off the oxychloride and washing with water feebly acidified with acetic acid, it is dissolved in 1 : 1 nitric acid. The solution is diluted, and the excess chloride determined as described under chloride and under silver.

Arsenic.—Tervalent arsenic may be titrated with bromate or with permanganate. In the former case the solution should contain at least 5 per cent free hydrochloric acid. In the latter case about 1 gm. sodium chloride per 100 ml., and a trace of iodide or iodate, should be added as catalyst. Indicator electrode: platinum.

Antimony.—Tervalent antimony may be titrated in the same manner as tervalent arsenic.

Tin.—Stannous tin may be titrated in the presence of sulphuric acid by means of permanganate. It may also be titrated by means of iodine. Indicator electrode: platinum.

Lead.—Lead may be determined by precipitation as ferro-

cyanide in the presence of ferricyanide (see p. 38). The use of a tenth molar ferrocyanide titrant containing 1 gm. ferricyanide per litre is recommended. The presence of acetates must be avoided. The minimum concentration of the lead should be 0·04N, and the titrate should be neutral. Indicator electrode: platinum.

Cadmium.—Cadmium may be determined on the same principles as lead. Sodium ferrocyanide containing a small amount of ferricyanide, used as titrant at about 75° C., is said to give the best results. The solution should be neutral. Indicator electrode: platinum.

Cadmium may also be titrated by precipitation as sulphide by means of Na_2S in a neutral solution to which 30 ml. 2N sodium acetate have been added. Indicator electrode: silver sulphide.

Zinc.—Zinc may be determined by means of ferro-plus ferricyanide in a manner similar to lead and cadmium. An N/10 solution of potassium ferrocyanide containing about 1 gm. ferricyanide per litre is employed as titrant, the titrate solution being at about 65° C. The results are said to be about 1 per cent below the theoretical. The ferrocyanide solution must therefore be standardized against a zinc solution. Indicator electrode: platinum.

Zinc may also be titrated as sulphide. Indicator electrode: silver sulphide.

Nickel.—Nickel may be titrated with a standard cyanide solution, the complex ion $Ni(CN)_4^{--}$ being formed. About 5 to 10 gm. sodium tartrate are added to the titrate to prevent the precipitation of $Ni(CN)_2$. Indicator electrode: silver sulphide.

Cobalt.—Cobalt may likewise be titrated with potassium cyanide, but in this case the inflexion point occurs when five CN radicals have entered into combination. The ion $Co(CN)_5^{---}$ readily undergoes oxidation; the titration should therefore be carried out very rapidly, or in hydrogen or other indifferent gas. Indicator electrode: silver sulphide.

Iron.—Iron is always determined by oxidation or reduction reactions. The indicator electrode is thus always platinum.

For the determination of ferrous iron, bromate, bichromate, or permanganate may be employed. To obtain a good inflexion point with the two first-named, a large excess of hydrochloric acid should be present. For the bromate titration the

titrate should contain an amount of concentrated hydrochloric acid corresponding to at least one-eighth, for the bichromate titration to at least one quarter of its volume. The permanganate titration is said to yield accurate results even in the presence of moderate amounts of chloride. Thus, according to Müller and Möllering (*Z. anorg. Chem.*, 1924, **141**, 111), the titration may be performed in hydrochloric acid solution of 0·4N strength.

For the determination of ferric iron either titanous or stannous chloride may be used as titrant. A hydrochloric acid solution should be employed, and the minimum temperature necessary for rapid reduction is given as about 55° C. in the former, and about 75° in the latter case.

Chromium.—Chromic compounds are usually prepared for titration by oxidizing them to the chromate state. For this purpose they may be boiled with a suitable amount of a solution of ammonium persulphate containing a small amount of silver nitrate in acid solution, the boiling being continued until all the persulphate has been destroyed. The chromic acid is then titrated in the cold either with a standard ferrous or with a standard stannous solution. As stated under iron, the titrate should contain about 25 per cent of its volume of concentrated hydrochloric acid. The presence of nitrates should be avoided. Indicator electrode: platinum.

Manganese.—Manganese compounds are oxidized to permanganate in a similar manner to that described for the oxidation of chromic compounds to chromate. To prevent decomposition of the permanganate formed, boiling must be discontinued as soon as the persulphate has been destroyed, a stage that is marked by incipient bumping of the solution. The titrant here employed is oxalic acid, the temperature being about 70° C. A considerable concentration of acid is also necessary in this instance. Indicator electrode: platinum.

Vanadium.—Vanadium compounds are oxidized to vanadate in a similar manner to that applicable to those of chromium and manganese. They may then be titrated in the cold by standard ferrous or stannous solution. It is also important in this case to have the titrate strongly acid. Indicator electrode: platinum.

Molybdenum.—The molybdenum as molybdate is titrated with a powerful reducing agent. Stannous chloride may be employed. To the titrate is added a volume equal to its own of concentrated

hydrochloric acid and one-tenth to one-twentieth gram of ferrous ammonium sulphate as a catalyst. A temperature slightly above the ordinary is employed. The inflexion point occurs when the hexavalent molybdenum has been converted to the quinquevalent state. Indicator electrode: platinum.

Cerium.—Cerium compounds are usually oxidized to the ceric state by boiling in not too acid solution with persulphate as described for chromium. The solution is acidified further, and titrated hot with oxalic acid. Indicator electrode: platinum.

Titanium.—Titanium compounds are usually reduced in a Jones reductor to the titanous (tervalent) state, and may then be oxidized to the quadrivalent state by any suitable standardized oxidizer such as bichromate. Indicator electrode: platinum.

Anions

Chloride, bromide, iodide, cyanide, sulphocyanide, and sulphide are titrated with silver nitrate, the titration being the reverse of that described under silver. As is familiar the titration of cyanide leads to two jumps, one at half equivalence, corresponding to the formation of the $Ag(CN)_2^{--}$ ion, the second to the complete precipitation of the cyanide as AgCN. Sulphide should be titrated in a solution strongly buffered with acetate, a silver sulphide indicator electrode being employed. For the other anions mentioned, either a silver or the corresponding indicator electrode of the second order may be used. For cyanide an Ag_2S electrode is very suitable (see p. 37). For the titration of bromide, iodide, and sulphocyanide as reductant anions see p. 38.

Sulphate is best determined by converting it into benzidine sulphate. For this purpose it is precipitated from a concentrated solution by means of a small excess of standard tenth molar benzidine solution containing about 3 per cent hydrochloric acid. After settling, it is filtered off and washed with a small amount of water. The filtrate is further acidified with about 10 ml. concentrated HCl and diluted to 100 ml. The excess benzidine in it is determined at 60° by means of a standard nitrite solution, a platinum indicator electrode being employed. 1 mol benzidine is equivalent to 1 mol H_2SO_4 and to 2 mols nitrite (Atanasiu and Velculescu, *Z. anal. Chem.*, 1932, **90**, 337).

Fluoride.—According to Allen and Furman (*J. Amer. Chem. Soc.*, 1933, **55**, 90) fluorides are titrated with cerous nitrate, whereby they are converted into cerous fluoride CeF_3. Excess of cerous salt is detected by means of a suspension of cerous potassium ferrocyanide (about 10 mg.) and about 0·25 ml. of a 0·1 per cent solution of potassium ferricyanide. The excess titrant liberates ferrocyanide from the suspension, the equilibrium of which with the ferricyanide causes a jump in the electrode potential. The titration is carried out in an approximately 50 per cent aqueous alcoholic neutral solution at about 70° C.

Oxidant Anions.—In the cases to be described a platinum indicator electrode is always employed.

Permanganate and Chromate.—The titration of these acids has been described on p. 42 in connexion with the determination of chromium and manganese.

Persulphate.—This acid may be titrated slowly at 50° C. with $FeSO_4$ in the presence of a trace of KI as catalyst.

Caro's acid.—Caro's acid is titrated with $FeSO_4$ in acid solution in the presence of manganese sulphate as catalyst.

Iodate and Periodate.—Both these acids are titrated with KI in a solution containing free sulphuric acid. Chlorides must be absent.

Bromate.—Bromate may be titrated with arsenious oxide in a solution strongly acidified with hydrochloric acid.

Chlorate.—Chlorate may be titrated with titanous sulphate or chloride in a sulphuric acid solution of normal to four times normal strength.

Hypobromite and Hypochlorite.—These acids are titrated with arsenious oxide in alkaline solution of half to normal hydroxylion strength.

Ferricyanide.—This may be titrated with sodium arsenite, antimonite, or stannite in the absence of air in a solution containing about 50 per cent NaOH at 70° C.

Reductant Anions.—Here the indicator electrode is likewise platinum in all cases.

Bromide.—According to Willard and Fenwick (*J. Amer. Chem. Soc.*, 1923, **45**, 623), bromides may be titrated with permanganate in a solution obtained by adding 5 ml. of a 10 per cent

KCN solution, and 5 ml. HCl of density 1·19 to each 10 ml. original titrate.

Iodide and sulphocyanide may be titrated with permanganate in a solution acidified with sulphuric acid.

Oxalate.—Oxalates may be titrated with permanganate in sulphuric acid solution at 70° to 80° C.

Hydrogen peroxide is titrated at ordinary temperature in acid solution with permanganate.

Ferrocyanide may be titrated in strongly acid solution with permanganate.

Sulphite may be titrated with hypobromite in slightly alkaline solution.

Hydrosulphite is titrated in the absence of air in alkaline solution with ferricyanide. It is thus oxidized to the sulphite stage.

Titration of several Radicals present in the same Solution.

The determination of more than one radical in a given solution by the same titrant by means of several inflexion points has been discussed in Chapter I. In many cases several radicals present in the same solution may also be determined by using successively different titrants for separate portions of the solution. Thus from a solution containing both silver and lead the silver may first be precipitated at high temperature as bromide using a silver indicator electrode, and the lead may then be determined as described above by means of a ferrocyanide titrant.

Example of the Analysis of an Industrial Alloy by means of Potentiometric Titration.—We describe here the determination of manganese, chromium, and vanadium in a steel (Hiltner and Marwan, *Z. anal. Chem.*, 1932, **91**, 401. See also Kelley and collaborators, *Ind. Eng. Chem.*, 1916, **8**, 722; 1919, **11**, 633; 1921, **13**, 939 and 1053). 1 gram of the sample is dissolved in 45 ml. H_2SO_4 (1 : 4) with heating. The residue of carbon and silicon is filtered off and washed with 50 ml. hot water acidified with sulphuric acid. The filtrate contained in a 500 ml. beaker is oxidized by boiling with 30 ml. ammonium

persulphate solution containing 500 gm. persulphate per litre of water and 10 ml. silver sulphate solution containing 5 gm. per litre. Boiling is continued until all evolution of oxygen has ceased, and bumping of the solution has begun. This shows that the excess persulphate has been completely destroyed. The permanganate is then titrated hot with N/50 sodium oxalate, a platinum indicator electrode being employed. The end of the titration, which should be carried out slowly, is taken as the point at which the potential has again become constant after the jump. After cooling, the sum of chromium and vanadium is determined by titration with fiftieth to one-tenth normal ferrous sulphate. It may be advisable to titrate beyond the end-point and titrate back with fiftieth normal permanganate. The solution now contains the chromium in the tervalent and the vanadium in the quadrivalent state. It is then heated to between 70° and 80° C., and titrated at this temperature with N/50 permanganate to completion of the jump in potential. The vanadium alone is oxidized to the quinquevalent condition.

Literature.

For further information on potentiometric titration we refer to the following books:

1. I. M. Kolthoff and N. H. Furman: *Potentiometric Titrations*, publ. Wiley & Sons and Chapman & Hall, 1931.

2. W. Hiltner: *Ausführung potentiometrischer Analysen*, Berlin, 1935.

3. E. Müller: *Die elektrometrische Massanalyse*, Dresden and Leipzig, 1932.

Much of the information contained in the preceding chapter is based on data given in Hiltner's book, to which reference is made particularly for the analysis of industrial products.

SECTION II

Conductimetric Analysis

CHAPTER I

THEORY AND SOME APPLICATIONS

Conductivity measurements are applied in chemical analysis in two ways, firstly as single measurements, and secondly in titrimetry to determine the end-point of a titration from a number of readings made at pre- and at post-equivalence. As instances of the former application we have particularly the determination of impurities in solution. Thus control of boiler feed water and of water used for numerous other purposes may be mentioned. Traces of cooling water which have leaked into a steam condenser are at once detected by resistivity measurement of the condensed water. In the sugar industry conductivity measurements are carried out to control the quality of syrups and molasses. In agricultural chemistry the conductivity of soil extracts is of importance. Milk, alcohols, and strong acids are examples of liquids to which conductivity measurements have been applied. Continuous works control of aqueous solutions is often operated by conductimetric apparatus. The moisture content of wood, textiles, and other solids has been estimated conductimetrically. Usually, however, the measurement of dielectric constants has been found more suitable for this purpose.

Conductivity Titrations

The basis of conductivity titrations is Kohlrausch's law of the independent migration of ions (Vol I, p. 22), according to which the " equivalent conductance " of a strong electrolyte at great dilution is the sum of the " equivalent conductances " or " mobilities " of its ions, and hence the " conductivity " or " specific conductance " of a dilute solution of strong electrolytes is equal to the sum of the mobilities of the individual ions each multiplied by its equivalent concentration. In the following table we give the mobilities of some of the more important ions at 18° C., the unit used being

$$\overline{\text{ohm} \times g\text{-equivalent}}$$

H^+	Li^+	Na^+	K^+	NH_4^+	Ag^+
315	32·5	42·6	63·65	63·6	53·25

$\frac{1}{2}Mg^{++}$	$\frac{1}{2}Ca^{++}$	$\frac{1}{2}Ba^{++}$	$\frac{1}{2}Cu^{++}$	$\frac{1}{2}Zn^{++}$	$\frac{1}{2}Pb^{++}$
44·6	50·4	54·4	45·3	45·0	60·5

OH^-	F^-	Cl^-	I^-	NO_3^-	CH_3COO^-
174	47·6	66·3	66·9	62·6	35

ClO_3^-	HS^-	HCO_3^-	$\frac{1}{2}SO_4^{--}$	$\frac{1}{2}CO_3^{--}$	$\frac{1}{2}C_2O_4^{--}$
55·8	57	39	68·7	60·5	62·4

It is seen from the table that whereas most mobilities are in the neighbourhood of 60, those of the hydrogen and hydroxyl ions occupy exceptional positions, the former being about five times, the latter about three times as large as most of the others. Advantage is frequently taken of this fact in conductimetric analysis, and also of the exceptionally low value belonging to the lithium and to the acetate ion. The temperature coefficient is in most cases between 2 and 2·5 per cent per degree.

Neutralization of a Strong Acid by a Strong Base.

We take as a first example of a conductivity titration the neutralization in very dilute solution of a strong acid by sodium hydroxide represented by the equation

$$H^+ + (Na^+) + (OH^-) \rightarrow H_2O + Na^+.$$

To distinguish the titrant added we are using round brackets. It will be seen that during pre-equivalence H^+ disappears, and an equivalent amount of Na^+ takes its place. If therefore at an arbitrary stage of the titration during pre-equivalence the conductivity is κ_0 and t equivalents of titrant Na^+ and OH^- ions have been added per unit volume of titrate, and if l_H and l_{Na} indicate the mobilities of the hydrogen and the sodium ions, then, assuming complete ionization and no alteration in volume to take place, the conductivity of the titrate becomes $\kappa_1 = \kappa_0 - l_H t + l_{Na} t$. If, however, the t equivalents of titrant occupied the volume v_n, and the original volume of the titrate was v_e, then the resulting conductivity will not be κ_1, but assumes a value κ_2 which is connected with κ_1 by the equation $\kappa_2 = \kappa_1 \cdot \dfrac{}{v_e + v_n}$. We therefore see that if changes of volume of the titrate may be neglected, the conductivity of the titrate goes down proportionally to t, and the graph representing the relation between t and κ_1, or between the titrant added and κ_1, is a straight line. On the other hand, if v_n is not small compared with v_e, the graph will deviate somewhat from a straight line. In order to avoid this, it is customary to make the titrant 20 to 100 times as concentrated as the titrate, using, say, about 100 ml. of the latter and placing the former in a 5-ml. microburette, graduated, say, in fifteenths or in hundredths ml., on which readings to about one- or two-thousandths ml. may be made.

In the instance we are considering, l_H being greater than l_{Na}, the pre-equivalence line slopes downwards. At post-equivalence, however, we have for the conductivities κ_0 and κ_1 the relation $\kappa_1 \qquad t(l_{Na} + l_{OH})$, l_{OH} being the mobility

of the hydroxyl ion. The post-equivalence graph is thus a straight line sloping upwards, and the equivalence point may be found as the point of intersection of two straight lines. In the present case it is also the lowest point of the composite graph. It would, however, be a mistake to assume that a minimum point or a maximum change of curvature is always identical with the equivalence point.

Instead of conductivities, any quantities that are proportional to them, such as suitable galvanometer readings, may be taken. Fig. 1 represents a neutralization of the kind we have considered. The neutralization of a strong base by a strong acid is analogous. These reactions illustrate some of the characteristic features of conductivity titrations. In contrast to other forms of titration no attempt is usually made to ascertain the end-point directly, but it is determined graphically from readings usually taken some distance from it during pre- and post-equivalence. It will be realized that graph paper and drawing implements are required, and it is necessary for the analyst to reconcile himself to the use of these possibly unfamiliar tools. An advantage of conductivity titrations arising not only from the ease and accuracy of the measurements, but also from the fact that the theory postulates infinitely dilute solutions, is that they can be operated at great dilution, and as a result they promise to become increasingly important in microchemical work.

Fig. 1.—Neutralization of Strong Acid by Strong Base

Neutralization of a Strong Acid by a Feeble Base.

Another fundamental advantage of conductivity titrations will become apparent on considering the example of the neutralization of a strong acid by a feeble base or the analogous one of the neutralization of a strong base by a feeble acid. We assume the base to be so weak that it may be considered

practically non-ionized, also its salts to be completely ionized. The neutralization is then represented by the equation

$$H^+ + (BOH) \rightarrow H_2O + B^+.$$
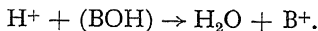
As is familiar, this process is appreciably reversible, the opposite reaction being known as hydrolysis and being governed by the equilibrium equation

$$\frac{[H^+][BOH]}{[B^+]} = K_h$$

in which the hydrolysis constant K_h represents an extremely small concentration. Therefore so long as the titrate reactant H^+ is in excess, the titrant re-actant BOH has an extremely small concentration, comparable in magnitude with the hydrolysis constant. This means that the titrant is used up almost quan-titatively throughout the titration everywhere except near the end-point, where the concentration of the titrate reactant H^+ becomes very small. The pre-equivalence curve is thus a straight line except near the end-point, where it merges into the post-equivalence line. The latter being also straight, the end-point is found as the point of inter-section of two straight lines drawn through points determined on the pre-equivalence and the post-equivalence branches. Fig. 2 represents a titration of the kind we have considered.

Fig. 2.—Neutralization of Strong Acid by Feeble Base

Neutralization of a Feeble Acid by a Feeble Base.

We have seen that conductivity titrations are superior to other methods of analysis in the fact that they are independent of the reaction proceeding quantitatively to a finish. This is exemplified in striking fashion by the titration of a feeble acid by a feeble base and vice versa, a process expressed by the equation

$$HA + (BOH) \rightarrow A^- + B^+ + H_2O.$$
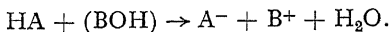
Although the end-point cannot be identified with any general property, and the process is therefore unsuited to the application of ordinary chemical means of analysis, yet perfectly good results may be obtained in many cases by conductivity titration, a graph of the form shown in fig. 3 being found. The slight downward curvature at the beginning of the neutralization represents the removal of hydrogen ions the presence of which may make itself felt, so long as A⁻ ions are absent.
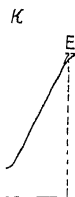

Fig. 3.—Neutralization of Feeble Acid by Feeble Base
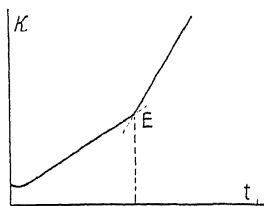
Fig. 4.—Neutralization of Feeble Base by Strong Acid

Neutralization of a Feeble Base by a Strong Acid and vice versa.

It is interesting to note that in conductivity titrations the rôle of titrate and titrant cannot as a rule be reversed without changing the character of the graph completely. Thus if in the titration of a strong acid by a feeble base we exchange titrate and titrant, we obtain a process expressed, e.g., by the equation

$$BOH + (H^+) + (Cl^-) \rightarrow B^+ + Cl^- + H_2O.$$
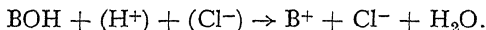
This is represented by a graph such as that shown by fig. 4, which it will be seen is entirely different in character from fig. 2. Owing to the obtuse angle of intersection of the pre- and post-equivalence lines, it is here more difficult to locate the end-point accurately. Here as in fig. 3 a slight downward curvature is indicated at the beginning of the titration to represent the removal of hydroxyl ions that may make their presence felt before they have been removed by B^+ ions.

Example of a Precipitation Reaction.

Precipitation reactions are in many cases suited to the application of conductimetric methods. We take as an example the titration

$$Cl^+ + (Ag^+) + (NO_3^-) \rightarrow \underset{\text{solid}}{AgCl} + NO_3^-.$$
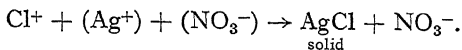
It will be seen that the net result of this reaction before equivalence is the replacement of chloride by the somewhat less mobile nitrate ion; therefore a slight slope downwards of the conductivity line takes place. After equivalence there is the increase due to the addition of both Ag^+ and NO_3^- ions, so that the graph has the general form shown by fig. 5. The reaction is slightly reversible owing to the solubility of the silver chloride, and throughout the whole titration the process is governed by the relation $[Ag^+][Cl^-] = K_{AgCl}$, in which the solubility product K_{AgCl} is very small. It will be seen that the concentration
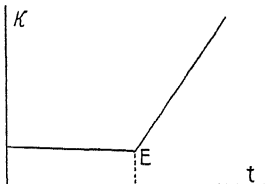
Fig. 5.—Precipitation Reaction

of titrant Ag^+ is extremely small during pre-equivalence, so long as the concentration of titrate Cl^- is appreciable; similarly during post-equivalence the concentration of titrate Cl^- is extremely small, so long as the concentration of titrant Ag^+ is appreciable. Thus, at a small distance from the end-point, the solubility of the precipitate does not interfere with the straightness of the titration lines, and the end-point may be found accurately by producing these to intersection. Where a precipitate is appreciably soluble, the pre- and post-equivalence branches merge into each other in a curved connecting piece, but it will be realized that precipitation reactions may be utilized in conductimetric analysis in cases in which the solubility of the precipitate would make the application of other methods impossible. It is claimed that good results may be obtained for a uni-univalent pre-

cipitate, so long as the original concentration of the titrate is more than ten times the solubility of the precipitate (Jander and Immig, *Z. Elektrochem.*, 1937, **43**, 212). In our discussion we have assumed that all salts are completely ionized, an assumption which by no means has universal validity; univalent ions should be preferred where possible.

Certain difficulties are inherent in the application of precipitation reactions. Thus supersaturation may lead to slow precipitation. This may be met by vigorous stirring and also by independent addition of the precipitate to the solution, as suggested by Van Suchtelen and Itano (*J. Amer. Chem. Soc.*, 1914, **36**, 1793). Reduction of solubility of the precipitate is also sometimes achieved by the addition of alcohol. Inaccurate results may further arise through the formation of basic salts and from other deviations of the reaction from the chemical equation assumed. Finally, adsorption of titrate or titrant ions on the precipitate may take place. Even when interfering circumstances make a precipitation deviate from the chemical equation, they do not necessarily make it inapplicable to chemical analysis. Thus the precipitation of sulphate in aqueous alcoholic solution by barium acetate does not conform strictly to the chemical equation. Nevertheless this reaction yields accurate results if the titrant barium acetate solution is standardized against a sulphate solution.

Displacement Reactions.

Displacement reactions may in many cases be usefully applied in conductimetric analysis. The displacement of ammonium or substituted ammonium radicals by sodium is a case in point. The titration of an ammonium salt by sodium hydroxide expressed by the equation

$$NH_4^+ + (Na^+) + (OH^-) \rightarrow NH_4OH + Na^+$$
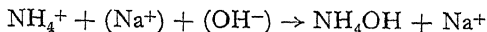
yields a graph such as that shown in fig. 6 resembling fig. 5. The pre-equivalence branch here slopes down slightly owing to the replacement of the more mobile NH_4^+ by the less mobile Na^+ ion, while the post-equivalence branch slopes upwards

proportionally to the titrant added. A curvature at the merging of the pre- and the post-equivalence lines is due to slight ionization of ammonium hydroxide during low concentration of both ammonium and hydroxyl ions.

P. Dutoit and Meyer-Levy (*J. Chim. Phys.*, 1916, **14**, 353) and I. M. Kolthoff (*Konduktometrische Titrationen*, p. 50) have applied conductivity titrations to the estimation of alkaloids in their salts. The displacement of a feeble by a strong acid is obviously analogous to that of a feeble base by a strong one. It is interesting to note that in displacement reactions the strength of the acid associated with the feeble base or vice versa is of no importance, so long as the salt may be considered completely ionized. Thus a salt such as ammonium acetate may be titrated either with a strong base or a strong acid.
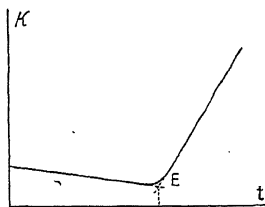
Fig. 6.—Displacement Reaction

Titration of moderately Strong Acids or Bases.

An important application of displacement titrations was made by Righellato and Davies (*Trans. Faraday Soc.*, 1933, **29**, 429) to the titration of a moderately strong acid. The neutralization of such an acid cannot be expressed by a single ionic equation, and hence a straight-line titration curve is not obtained. This difficulty was overcome by converting the acid partially into its ammonium salt, and then titrating the mixture with sodium hydroxide. Thus in the titration of mandelic acid, ammonia was added sufficient to neutralize about a third of the acid, and the titration was then performed with standard sodium hydroxide. A composite titration curve such as that shown in fig. 7 was obtained. The
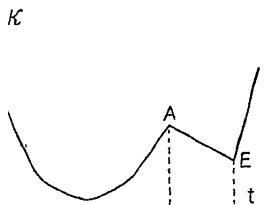

Fig. 7.—Titration of Mandelic Acid

NaOH added to the point A is utilized in the neutralization of the free acid remaining after addition of the ammonia, the initial drop in the curve being due to the removal of hydrogen ions, an effect which is later swamped by the increase in conductivity arising from the ions due to salt formation. Further NaOH after the point A is used up in replacing the ammonium by the sodium ion, until the equivalence point E is reached.

The Titration of Mixtures

Mixture of a Strong and a very Weak Acid.

Both constituents may easily be determined in one titration in a mixture containing a strong and a very feeble acid. If neutralized by ammonia, a composite curve derived from figs. 2 and 3 and represented in fig. 8 is obtained. The titration to the point E_1 represents the neutralization of the strong, that between E_1 and E_2 the neutralization of the weak acid. During most of the titration to the point E_1, the excess of the strong acid prevents ionization of the weak acid, near E_1; however, as explained in connexion with fig. 3, ionization of the weak acid may produce a deviation from the straight line E_1E_2. This does not interfere with the determination of E_1 as the point of intersection of two straight lines, so long as a sufficient portion of the line to E_1 remains linear. When, however, only a very small amount of strong acid is originally present, it may be necessary to add a known amount, in order to obtain the straight portion of the curve, and find the amount originally present by difference. This method has been used by Kolthoff (*Rec. trav. chim.*, 1920, **39**, 280) to determine the mineral acid content of vinegar, and by Righellato and Davies (*Trans. Faraday Soc.*, 1933, **29**, 437) to determine free sulphuric acid in leather extracts.

Other Mixtures.

Among other mixtures to which conductivity titrations have been applied in order to estimate two constituents in one

operation, we mention solutions containing an acid and the salt of a feeble base. The acid may be either strong, of moderate strength, or weak. The titrant in each case is sodium hydroxide. Corresponding mixtures in which the rôles of acid and base are interchanged may, of course, be correspondingly estimated.

Mixtures of NaOH and Na_2CO_3 titrated with a strong acid yield a graph of the general form shown in fig. 9. The neutralization of the NaOH ends about A. Then follows the conver-
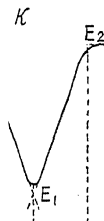

Fig.8.—Mixture of a Strong and a very Weak Acid
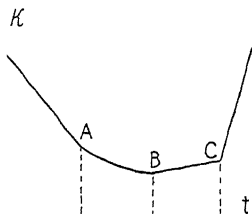
Fig. 9.—Alkali mixtures titrated with Strong Acid

sion of carbonate into bicarbonate till about B according, e.g., to the equation

$$CO_3^{--} + (H^+) + (Cl^-) = HCO_3^- + Cl^-,$$
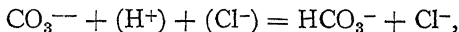
and then the neutralization of the bicarbonate from B till C according to

$$HCO_3^- + (H^+) + (Cl^-) = H_2CO_3 + Cl^-.$$
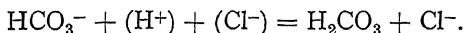
The point C representing the total amount of alkali is usually found with sufficient accuracy by entering as many points as possible in the curved portion. Graphs of the kind shown have been employed for analytical purposes by W. D. Treadwell, *Helv. Chim. Acta*, 1925, **8**, 89; and M. Auméras and J. Marcon, *Bull. Soc. chim.* (4), 1932, **51**, 1594.

Titrant Sodium Hydroxide Solution containing Carbonate.

When titrant alkali hydroxide contains carbonate, carbonic acid collects in the titrate solution, usually saturating it, and is neutralized after the end of the titration. Thus a slight error, say of 0·1 ml., is produced, which is proportional to the volume of the titrate but independent of the amount of acid ion originally present. According to Jander and Pfundt (*Leitfähigkeits Titrationen*, p. 61), it usually suffices to wash the sodium hydroxide sticks with water free from carbonic acid, and make up the titrant with such water, protecting it from the carbon dioxide of the air by means of a soda-lime guard tube.

Dibasic Acids.

As stated in connexion with potentiometric titrations, dibasic acids yield consecutively a univalent and a bivalent negative ion, and when titrated, say, with ammonia, may yield a titration graph, in which the two stages can be disentangled. Oxalic acid is a case in point. Usually, however, the first stage cannot be sharply separated from the second.

Applications of Conductivity Titrations and General Remarks.

In addition to the applications already mentioned, conductivity titrations have been employed with advantage in the examination of beer and wine, fruit juices, milk, drinking water, urine, and other liquids. They have been employed in the manufacture of hydrogen to determine its carbonic oxide content. They have found application in the sugar, the paper, the colour industry, and in agricultural analysis. For a review of applications reference is made to an article by J. Grant in the *Industrial Chemist* of 1934, p. 391.

Conductimetric titrations are, as already stated, of special importance in the titration of very dilute solutions, and in cases where the reversibility of a reaction makes the application of other methods impossible. Thus they lend themselves

particularly to microestimations.   Like potentiometric titra-
tions they are unaffected by the colour of the titrate.   As a
rule the end-point is found graphically, the titration lines
being drawn to pass as near as possible to the maximum
number of available points.   For the determination of the end-
point by calculation from a number of readings, reference is
made to a paper by J. Mika (*Z. anal. Chem.*, 1936, **106**, 248).
Only in rare cases, as in the determination of sulphate, can
the graphical method be dispensed with, and be replaced by
the determination of a minimum in the titration curve.   In
conductivity titrations the presence of foreign electrolytes is
a cause of difficulty, although, as will be seen in the next
chapter, titrations have been performed in solutions contain-
ing a very large excess of foreign electrolytes.

APPARATUS AND MEASUREMENTS

As is familiar, a difficulty inherent in the measurement of electrolytic resistances and conductivities is due to polarization of the electrodes. This difficulty was overcome by Kohlrausch in 1879 by the introduction of alternating current in which equal and opposite pulses neutralize each other, the polarizing effect of a single pulse being small enough to be negligible. Expressed in greater detail, each pulse may be assumed to produce a polarization proportional to the amount of current that has passed through the electrode, the latter thus acting as a condenser. The whole cell therefore behaves to alternating current as a resistance in series with a large capacity. By a familiar equation of electro-technics the apparent resistance or impedance Z is connected with the true resistance R for sinusoidal alternating current having an angular frequency ω by the equation

$$Z^2 = R^2 + \frac{1}{C^2 \omega^2},$$

where C is the polarization capacity of the electrode. C is proportional to the effective area of the electrode. From this equation we calculate that with sufficient accuracy the relative error

$$\frac{Z - R}{R} \qquad \frac{1}{a^2 R^2 f^2},$$

where a is proportional to the effective area of the electrode, R is the resistance of the cell, and f the frequency of the alternating current. It must not be forgotten that if our assumption is to hold good, that the electrode behaves as a

condenser of constant capacity, then the current must be kept small. If the unknown resistance placed in one of the arms of a Wheatstone bridge contains capacitance or inductance, a sharp balance point can only be obtained if these are suitably balanced out either by a capacitance or an inductance placed in one of the other arms of the bridge. In conductivity titrations, however, it has not been found necessary to adopt these devices.

Use of Continuous Current.

Where very large resistances are concerned, continuous current of high voltage may be employed, and the polarization may be assumed to acquire a constant value. Thus in the " Dionic water tester " of Digby and Biggs (*Trans. Faraday Soc.*, 1910, **6**, 167), made by Evershed and Vignoles, continuous current under a pressure of 100 volts is applied, the method of measurement being similar to that employed for insulation testing. A constant polarization is assumed, and an automatic temperature correction is applied by varying the length of the liquid column under test.

Accurate results in conductivity measurement have also been obtained with direct current by J. N. Brönsted and R. F. Nielsen (*Trans. Faraday Soc.*, 1935, **31**, 1478) by the use of an apparatus employing a long column of liquid and non-polarizable hydrogen electrodes (see also Rae, *J. Chem. Soc.*, 1931, 3143).

Use of Alternating Current.

As a rule alternating current is used. In former times this was always obtained from small induction coils. More recently these have been replaced by commercially obtainable valve oscillators (see Jones and others, *J. Amer. Chem. Soc.*, 1928, **50**, 1049; 1929, **51**, 240; 1931, **53**, 411; also Woolcock and Murray-Rust, *Phil. Mag.*, 1928, VII, **5**, 1130). Small independently driven alternators are also used for conductivity titrations, but more frequently the A.C. mains supply, with a frequency of 50 cycles, or a mains-operated oscillator yielding a frequency of about 1000 cycles per second is employed.

In both the last-named cases a transformer is interposed between the supply and the measuring system.

Conductivity Vessels.

We distinguish between vessels to be used only for titrations and those to be employed specifically for conductivity measurements. In the former case the vessels must be of sufficient size to hold the titrate; they shoul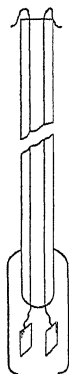d have vertically placed electrodes, so that precipitates or gas bubbles cannot settle on them. Frequently they are fitted with mechanically operated stirrers, and sometimes the electrodes are arranged at the side of the vessel, so as to be out of the way of the stirrer and the titrant supply. In all cases conductivity vessels must be designed so that when charged with the proper amount of electrolyte a further addition of electrolyte does not affect the conductance appreciably. When absolute values of conductivities are required, the so-called constant of the cell, which depends on its shape and size, must be determined. If the resistance of a liquid measured in the cell is R, and its specific conductance is κ, the cell constant k is defined by $\kappa = \dfrac{k}{R}$ or $k = \kappa R$.

Fig. 1.—" Immersion Type" Electrode Vessel.

Fig. 1a.—Electrode for Mullard Conductivity Bridge.

It may thus be determined by measuring the resistance of a liquid of known specific conductance in the cell, and may be defined as the specific conductance a liquid would have, whose measured resistance (or conductance) was found to be unity. Its dimension is cm.$^{-1}$. For types of conductivity

cell used only in scientific investigations we refer to books on physical chemistry.

Fig. 1 shows diagrammatically an " immersion type " electrode vessel designed for dipping into the test liquid. It will be seen that the electrodes are fitted into a pipette-shaped glass shield, open at the bottom and supplied with a hole at the top. Fig. 1a is a view shown of an electrode of this kind of robust construction which has been designed for use with the Mullard conductivity bridge (Vol. II, p. 6).
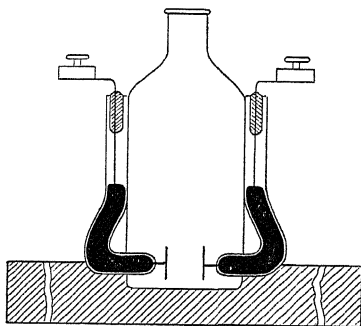

Fig. 2.—Conductivity Vessel
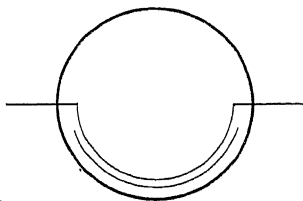
Fig. 2a.—Large Electrodes

Fig. 2 represents a type of vessel which has been very commonly employed in conductivity titrations. The connexion to the electrodes is made through a mercury junction which should be adequately protected from spilling, e.g. by sealing the leading-in wires with soft wax or other cement. The vessel should be provided with a stand, made, say, from a block of wood, to prevent it from being upset when not being manipulated. Mixing of titrant with titrate is effected by hand, the vessel being held by the neck, to avoid heating of the titrate. For low conductivity electrolytes large electrodes are sometimes placed close to each other on one side of the conductivity vessel, as shown in fig. 2a.

Fig. 3 shows a vessel constructed by the writer for use with his stands. It consists of a bottle with an ebonite lid which

should be turned to taper slightly more than the neck of the
bottle so as to avoid the risk of sticking. The electrodes
shown are platinum wires of about $\frac{1}{2}$ to 1 cm. length and 1 mm.
diameter. The guide-tube of the stirrer, which is fitted in
the lid, is held by the outer electrode clamp, and the stirrer
is operated by the inner electrode clutch. Instead of the
wires, plates may be employed. The design may be described
as a modification of one due to Britton
and German (*J. Chem. Soc.*, 1930, p. 1250).

Fig. 3.—Conductivity
Vessel

Fig. 4 shows a titration vessel designed
by Jander and his collaborators (G. Jander
and A. Ebert, *Z. Elektrochem.*, 1935, **41**,
790, and J. Harms and G. Jander, *Z.
angew. Chem.*, 1936, **49,** 106) for use with
electrolytes of high conductivity. It will
be seen that it is designed as a " circulatory
vessel ". It consists of a central tube with
a screw propeller, to which the circula-
tory system of side-tubes is attached, the
electrodes being placed at the extreme
opposite ends of the vessel. For series
analyses it may be fitted with a waste
tube closed by a ground-glass stopper and
attached to a rubber tube (fig. 4*a*). The
capacity of the vessel is about 35 ml., the
diameter of the electrodes 1·5 cm., and
their distance apart 10 cm. In the
sketch the writer has shown in dotted lines a cork and guide-
tube for the stirrer to render the apparatus suitable for use on
his stands.
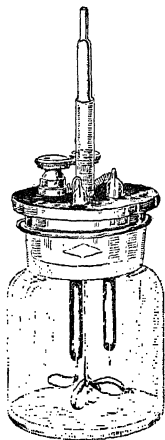
Platinizing and Cleaning the Electrodes.

Although small errors introduced by polarization tend to
cancel each other out in conductimetric analysis, care should
be exercised to keep the electrodes clean and efficiently
platinized. Polarization can usually be detected by the altera-
tion of results produced by altering the stirring efficiency.
The vessel and electrodes are first carefully cleaned with hot

sulphuric chromic acid mixture, and the electrodes are then plated from the " Lummer-Kurlbaum " solution containing 3 gm. chloroplatinic acid and 25 mg. lead acetate per 100 ml. The current may be obtained from two accumulators, the poles of which have been connected to the ends of a suitable sliding rheostat as in the electrolytic stands. The current is shunted from one of the ends and the slider, so as to produce a moderate evolution of hydrogen. Each electrode should be used alternately as anode and cathode, and plating should be
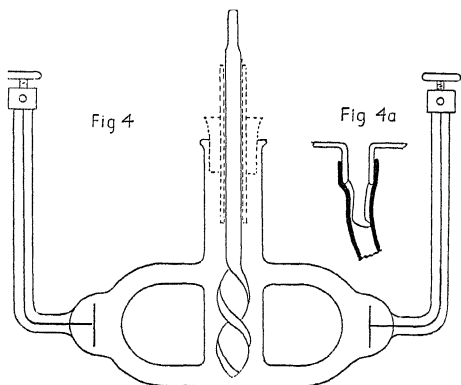
Fig. 4.—Titration Vessel designed by Jander

continued until both electrodes are covered with a jet-black deposit. The time may vary from about two to about five minutes. Platinizing solutions may be used even after their platinum content has gone down considerably, but they should be rejected if a velvety jet-black deposit is not obtained. After platinizing, the electrodes must be freed from traces of chlorine by cathodic treatment with dilute sulphuric acid. They must then be carefully washed in distilled water, and must always be stored in water. Platinum black tends to adsorb solutes. This may lead to errors when working with extremely dilute solutions. With electrolytes having a specific conductance of less than 10^{-3} ohms, it is recommended only

to roughen the electrodes slightly by preliminary treatment with aqua regia.

Temperature Control.

In most cases the conductivity of electrolytes increases by about $2\frac{1}{2}$ per cent per degree, and therefore constancy of temperature is essential during conductimetric titrations. Unavoidable causes of interference are the heats of reaction and heat produced by the current. These are reduced to a minimum by carrying out all titrations in dilute solution and employing as small measuring currents as possible. In titrating, great care should be taken that both titrate and titrant have attained laboratory temperature before use, and when additions of alcohol have to be made, previously diluted solutions must be employed which have had time to acquire the temperature of the laboratory. The latter should be as uniform as possible. For titrations in the presence of large amounts of foreign electrolytes, the vessel is placed in a large well-lagged trough of water which has acquired the temperature of the laboratory, and is gently stirred by mechanical means. The use of specially controlled thermostats would entail unnecessary complication. Titrations are sometimes performed at 0° C., ice-water mixtures being employed in the trough, and apparatus has also been described in which the titration vessel is jacketed by vapour from a boiling liquid (Jander and Pfundt, *Konduktometrische Analysen*, 2nd ed., pp. 37 and 38).

Burettes.

As stated on p. 49, the burettes usually have a capacity of 5 ml., and should be graduated in fiftieths of a millilitre, 1 ml. corresponding to a length of about 5 cm. They should have an extension drawn to a fine jet, readings being made just after a drop of titrate has left the tip of the burette. For micro-titrations the tip is usually placed below the level of the titrate, a burette graduated in 1/100 ml. being employed. Attention is drawn to a burette for micro-titrations described by Jander and Harms (*Z. angew. Chem.*, 1935, **48**, 267). It

is of Jena glass, having a perfectly uniform bore of 2·52 mm. The titrant is forced out by a piston of special steel provided with a leather washer. This is lowered or raised by means of a ratchet and wheel. The motion of the latter is read on a drum, which is graduated to read to 1/2000 ml. It is desirable to have burettes sealed to a reservoir of a capacity of, say, 200 ml., allowing them to be filled from below.

A.C. Circuits and Measuring Instruments for Use in Conductimetric Titrations.

The Wheatstone Bridge.

We propose to concentrate our attention on circuits the readings of which change proportionally with changes in the conductivity. In the Wheatstone bridge with slide-wire
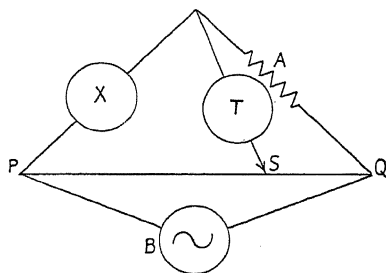
Fig. 5.—Wheatstone Bridge

represented in fig. 5 as used for resistance measurements, X is the unknown resistance, A a standard resistance of the same order of magnitude as X, PQ the slide-wire, S the slider. When the bridge is balanced $X : A = PS : SQ$, where the symbols represent the resistances of the items indicated. If the slide-wire is 1000 mm. long and of uniform resistance, PS and SQ may equally represent lengths of wire. Making

$PS = a$, and $SQ = 1000 - a$, we have $X = A \dfrac{a}{1000 - a}$.

Tables containing values of the function $a/(1000 - a)$, and

their logarithms, have been calculated by Obach (1879). In conductivity titrations it is changes proportional to changes in $1/X$ that are required. The constant value of A is therefore of no interest and may be omitted. It will also be seen that if the positions of X and of A in the Wheatstone bridge are exchanged, values proportional to $1/X$ will be obtained in carrying out normal calculations of resistance in which the ratio $PS : SQ$ is involved.

Instead of the slide-wire bridge shown in fig. 5, C. W. Davies (*Conductivity of Solutions*, p. 240) recommends the use of a special dial resistance box of the post-office type in which the branches A and SQ are each replaced by resistances of 100 ohms, and PS by a decade system possessing three dials which control respectively multiples of 10, 100, and 1000 ohms. The unit decade is replaced by a wire from which resistances between 0 and 10 ohms can be tapped off by means of a slider fitted with a pointer which indicates tenths of an ohm on a circular scale. In conductivity titrations it is possible to use the Davies box or an ordinary post-office dial resistance box in such a way as to obtain directly from the dials readings which are proportional to the conductivity of the test solution. The post-office box, as is familiar, is designed so as to give readings of resistances or power-ten multiples or submultiples of them directly on the box. For this purpose the place of the resistance PS of fig. 5 is taken by the standard variable resistance, whereas the places of SQ and A are taken by the ratio coils. If the readings of PS are to be proportional to conductances and not to resistances, X and A must be exchanged as already explained. Obviously it would be possible to make the alteration required in the box itself by connecting the resistance A to the point P instead of the point Q. In practice it will, however, be found simpler to use the resistance $SQ + A$ as a single unit, and to interpose between X and PS a constant resistance, for which purpose a duplicate titration vessel with titrate is very convenient. The necessary alterations in the connexions to the source of current and the null-point instrument must of course also be made.

A.C. Null-point Instruments for Use with the Wheatstone
Bridge. The Telephone, the Optical Telephone, and the
Vibration Galvanometer.

The telephone was first introduced into the technique of conductivity measurement by Kohlrausch in 1879, and most standard data have been determined by its means. In contrast to many devices for detecting alternating current, it is sensitive to extremely small current strengths. It is used preferably for frequencies of about 1000 per second. For low frequencies such as those of the supply mains, the optical telephone introduced by M. Wien in 1891, or the vibration galvanometer described by Rubens in 1895, may be employed.

The Cathode-ray Detector.

The cathode-ray detector described in Vol. II, p. 5, and the " Mullard measuring bridge " or " Philoscope " used in conjunction with it promise to become of great importance in the applications of conductivity measurements. The Mullard bridge is constructed to give direct readings of resistances and capacitances. The interchange of connexions discussed above can be made by the suppliers of the instrument, so that readings proportional to conductances instead of resistances are obtained. It must be noted, however, that owing to the construction of the bridge, an exchange of terminals is also involved in this, and an alteration in the capacity circuit, which makes it necessary to apply division instead of multiplication, when the bridge is used for capacity measurement. The bridge is shown in fig. 3a *loc. cit.* If required, an oscillator giving a frequency of 1000 per second, which is designed for attachment to the 50-cycle A.C. mains, can be obtained from the makers (*Philips Tech. Rev.*, 1938, **3**, 184).

The Sumpner Galvanometer, and Jander and Schorstein's
Circuit.

The Sumpner galvanometer is a development of the Siemens electrodynamometer. In the latter the current to be measured

is passed in series through a fixed coil and a movable one placed at right angles to it. The torque on the latter is proportional to the square of the current strength. The sensitivity of the instrument therefore approaches zero for zero current, a peculiarity common to many forms of alternating current meters such as those using thermocross junctions, &c. This objection was overcome by Sumpner (*Proc. Roy. Soc.*, A, 1908, **80**, 327) by passing an independent synchronous alternating current of constant strength through the fixed
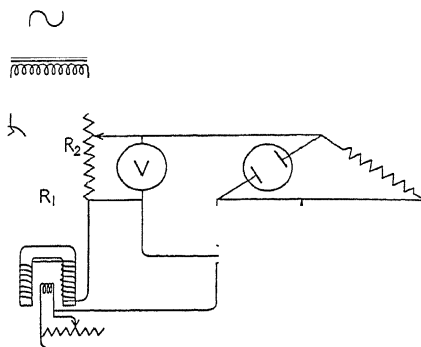
Fig. 6.—A.C. Mains Circuit designed by Jander and Schorstein

coil. The magnetic field of the latter was strengthened by the use of an iron core. Convenient pointer instruments based on this principle, having a linear scale, are now commercially obtainable. They have a sensitivity of about 1 division per 10^{-5} amp. and an internal resistance of about 25 ohms.

Fig. 6 shows the circuit due to G. Jander and H. Schorstein (*Z. angew. Chem.*, 1932, **45**, 701). It is designed for use on the A.C. mains. The current from the latter is taken through a 1 : 1 transformer. This acts as a protection against earth short-circuits, and if suitably designed, it also stabilizes the voltage of the measuring circuit. The current from the secondary passes through a barretter B and then back through the two rheostats R_1 and R_2, from which respectively a constant

voltage for the field magnet of the galvanometer and an adjustable voltage for the bridge, measurable by the voltmeter V, are tapped off. The barretter consists of an iron filament placed in a hydrogen atmosphere and constructed in the form of an ordinary incandescent lamp. The wire is kept incandescent during use. The purpose of the barretter is to keep the current steady during voltage fluctuations, its efficacy being based on the fact that any increase in the applied
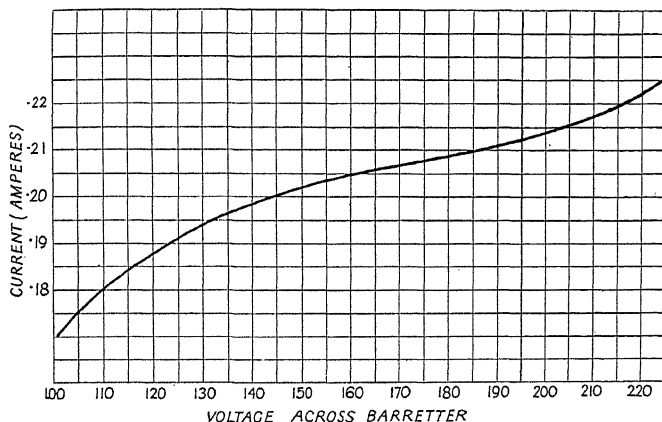
Fig. 7.—Osram Barretter

P.D. raises the temperature of the filament and thus its resistance, so that the current passing through it is kept practically constant. Barretters first became known in connexion with the Nernst incandescent lamp. In fig. 7 is shown a current-voltage curve for a commercial form of barretter. It will be seen that if a voltage of 160 is normally applied to this barretter, variations of 30 volts either way have little effect on the current of 0·205 amp., causing it to vary only from 0·195 to 0·210 amp. If the voltage at the transformer terminals is 225, the combined resistance of the rheostats R_1 and R_2 should thus be about (225–160)/0·205 or 317 ohms,

in order that a current of about 0·205 amp. should normally pass through the barretter. Fig. 6 shows that the sensitivity of the galvanometer is adjustable by means of a shunt.

Rotary Commutators.

The use of commutators for conductivity measurement was suggested by Fitzpatrick in 1886 (*Brit. Assoc. Report*, 1886, p. 328). A well-known form of commutator for conductivity measurement was described by W. C. D. Whetham in 1900 (*Phil. Trans.*, A, 1900, **194**, 332). Two rotary commutators were mounted on a common motor-driven axis. The first periodically reversed the current supplying the Wheatstone bridge, whereas the second synchronously reversed the galvanometer used as a detecting instrument, thus making its current unidirectional. A rotary commutator was also employed by W. D. Treadwell and S. Janett (*Helv. Chim. Acta*, 1923, **6**, 734) in a circuit to be described below. G. Jander and O. Pfundt (*Z. Elektrochem.*, 1929, **35**, 206, and *Chem. Fabrik*, 1929, **2**, 184) have described a circuit in which measuring current at about 4 volts is supplied to the Wheatstone bridge by a small alternator. On the axis of the latter a commutator is fixed, which reverses the connexions to the galvanometer synchronously with the alternations of the current. A mains-operated motor is coupled to the alternator, which, it is stated, delivers current of a voltage practically independent of fluctuations in the mains. With contemporary constant frequency of the mains, the use of a synchronous motor would completely eliminate the possibility of fluctuations on the terminals of the alternator.

Measurement of Changes in Conductivity by Proportional Changes in Galvanometer Readings.

Although readings on the Wheatstone bridge which are obtained by the use of a zero instrument may be made proportional to conductivities, yet there is a certain advantage in the direct employment of galvanometer readings in the titration graphs. The first successful attempt in this direction

was made by Treadwell and Janett (*loc. cit.*). These investigators placed a constant P.D. obtained from an accumulator battery across the series combination of titration cell plus D.C. measuring instrument. In this combination the titration cell only was connected to the circuit by means of a rotary commutator to avoid polarization. It is clear that if the resistances of the measuring instrument and of the commutator are negligible, the current passing through the circuit will be proportional to the conductance of the cell, but even when the resistance of the measuring device is one-tenth or more of that of the cell, the deviation from a straight line relation between conductance and galvanometer reading is not great, and results of considerable accuracy may be obtained in conductivity titrations.

Jander and Pfundt likewise recommend the direct use of galvanometer readings in titrations. Thus, when using the circuit shown in fig. 6, the Wheatstone bridge is set so as to give a convenient galvanometer reading at the beginning of the titration. Leaving all adjustments unchanged, the galvanometer readings are then plotted directly against volume of titrant in the titration graphs. It is obvious that in all direct-reading galvanometer circuits a constant applied voltage must be ensured.

The Use of Rectifiers in conjunction with Continuous Current Meters.

Simple circuits for use in conductivity titrations are obtainable by the use of rectifiers now made generally accessible by the radio industry. Leaving valve rectifiers aside for later reference, we here mention copper-cuprous oxide metal rectifiers, selenium rectifiers, carborundum rectifiers, and the cat's-whisker crystal detectors of former radio sets. The rectifying contact in such rectifiers is believed to be a three-stage composite layer consisting of the metal, an extremely thin non-conducting layer, say, of 10^{-5} cm. thickness, and a layer of a semi-conductor. Thus in the case of the copper-cuprous oxide rectifier there are: the copper, an extremely

thin layer of non-conducting pure cuprous oxide, and a layer of semi-conducting slightly oxidized cuprous oxide, i.e. of probably a solid solution of cupric in cuprous oxide. The action of the rectifier is electronic and is based on the greater ease with which electrons can pass from the metal through the thin non-conducting layer to the semi-conductor than in the reverse direction. For a discussion of the theory of metal rectifiers, which are also known as *blocking layer rectifiers*, the reader is referred to an article by W. CH. van Geel in *Philips Technical Review*, 1939, 4, 100.

An important advantage of metal rectifier units is that they can be employed in conjunction with existing D.C. measuring instruments. Thus conductivity titrations may be conveniently carried out with the unipivot galvanometer repeatedly referred to in this book. Self-contained instruments having the rectifier in the instrument case are also commercially obtainable. A unit of four rectifiers is generally used in which the rectifying elements are combined to form a "Graetz" bridge. Thus full-wave rectification is obtained, and there is no hindrance to the passage of the alternating current through the cell, as would be the case if half-wave rectification were employed. Fig. 8 represents the Graetz bridge attached to a shunted measuring instrument. The alternating current enters and leaves at the terminals A_1 and A_2. If A_1 is positive to A_2, there is a passage from A_1 through the rectifier 1 to B_1, thence through the instrument to B_2 and through the rectifier 3 to A_2, whereas when A_2 is positive to A_1 the path of the current is through rectifier 2, thence as before through B_1 and the instrument to B_2 and finally through the rectifier 4 to A_1.
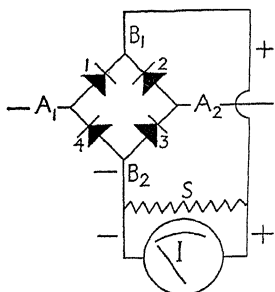
Fig. 8.—Graetz Bridge attached to a shunted Measuring Instrument

Bridges of about half an inch diameter and thickness are supplied by the Westinghouse Brake & Signal Co., Ltd., for

use with instruments reading up to 1 milliampere. Larger bridges are also made. For instruments using a smaller current, rectifiers described as " Westector " type W.1 may be obtained to order, which must be assembled to form a bridge. It is important to note that the terminals B_1 and B_2 must always be kept connected through a suitable resistance before the terminals A_1 and A_2 are connected to the current supply. If this is not the case the full supply P.D. will arise between A_1 and A_2 and the rectifier will almost certainly be destroyed. If the rectifier is not connected permanently to the instrument I, it should therefore be combined in a permanent unit with the shunt S. If we define the " apparent " resistance R of a rectifier to an applied P.D. E by the relation $R = \dfrac{dE}{dI}$, where I is the current, then metal rectifiers are characterized by the statement that for very low currents their apparent resistance is high, but on increasing the current it soon becomes constant, and the applied P.D.-current equation assumes the form $E = a + RI$. To obtain a linear relation between the applied P.D. and the current, each of these must therefore be made to exceed a certain value. The rectifier then behaves on further increase of current as an ohmic resistance R, to which not the P.D. E but the P.D. $E - a$ has been applied. Thus defined, the resistance of a rectifier bridge of the kind referred to above is usually between 300 and 400 ohms, the P.D. correction a being under 0·5 volt.

Lee's Circuit.

Fig. 9 represents a circuit used in the writer's laboratory by D. C. Lee. A somewhat similar circuit, in which, however, only half-wave rectification was employed, was described previously by T. Callan and B. Horrobin (*J. S. C. I.* (*T.*), 1928, **47**, 341). The circuit is designed so that alternating current is passed through the conductivity cell, the current strength being kept within the limits between which the rectifier may be used with apparently constant resistance. There is an arrangement by means of which the zero point on the scale

of the measuring instrument may be arbitrarily made to correspond to chosen values of the main current by the application of an opposing P.D. or bias. By suitable adjustment of a shunt resistance the whole scale may then be made available for indicating changes of conductance during a titration. It will be seen from the figure that current from a bell transformer, the primary of which has been connected to the A.C. mains, is passed through a shunt resistance arranged so that an arbitrary P.D. $E_m{'}$, between 0 and 8 volts,
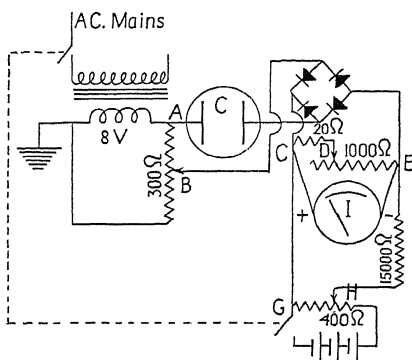
Fig. 9.—Lee's Circuit

may be tapped off between the points A and B. Starting from A, current passes through the cell C and one of the branches of the rectifying bridge to what may be described as the measuring part-circuit, and then through another branch of the rectifier back to B. The measuring part-circuit consists of the unipivot galvanometer or similar instrument I with its shunt CD + DE, CD being permanent and DE variable. The variable " bias " P.D. is tapped off from the points G and H and applied through a resistance shown as 15,000 Ω to the measuring instrument. A study of the circuit shows that the " bias current ", while opposing the current in the galvanometer, aids that flowing through the conductance cell. Further, owing to the fact that the rectifier bridge acts as a

reversing key when the alternating current reverses its direction, the effect of the " bias current " on the " test " current flowing through the cell is the same in magnitude, whether the latter flows in one direction or the other. Although distortion is thus produced, there is no destruction of symmetry which would lead to polarization. The part-shunt CD entered on the diagram as 20 Ω is chosen of such a value that when the sliders D and H are set so that the resistances DE and GH are made zero, convenient, previously ascertained readings are obtained on the galvanometer for the limiting currents to be employed during a titration, say, 200 and 1000 microamperes respectively. During the titration the current passing through the conductivity cell must be kept between these limits to ensure on the one hand an " apparent " constant resistance of the rectifier, and on the other absence of overloading. Before starting a titration the slider B determining E_m' is set so as to ensure that the current will lie between such limits. The part-shunt rheostat DE is calibrated so as to indicate positions for doubling the current-sensitivity of the galvanometer readings.

In order to formulate the relation between the current flowing through the measuring instrument and the other quantities characterizing the circuit, we indicate potential differences by E, currents by I, resistances by R, conductances by C, and use subscripts as follows: for the variable test liquid x, thus C_x is the conductance of the test liquid; for the main circuit m, thus E_m' is the P.D. between A and B, which is assumed constant; $E_m = E_m' - a$ is the same P.D. corrected as explained above by allowing for the rectifier constant, R_m is the resistance of the cell plus the " apparent " resistance of the rectifier, and C_m the reciprocal of R_m. For the rectifier r is used, thus R_r is its apparent resistance; for the measuring instrument with its shunt the subscript is s, thus I_s is the current passing through the combined unit, R_s is its resistance, and C_s its conductance. The subscript for the bias part-circuit is b, thus E_b is the P.D. between G and H, which is assumed constant, R_b is the resistance of the part-circuit shown as 15,000 Ω in the diagram, and C_b is the corre-

sponding conductance. Then the application of Kirchhoff's method leads to the results

$$I_s = \frac{E_m C_m - E_b C_b}{1 + C_b R_s + C_m R_s}$$

and

$$I_m = E_m C_m - I_s R_s C_m,$$

where

$$\gamma = \frac{C_x}{1 + C_x R_r}.$$

In the employment of the circuit it is desirable that the readings of the measuring instrument should as nearly as possible follow a relation which is linear to variations in the conductance of the cell. A study of the equations given for the calculation of I_s shows that this desideratum is attained by making the resistance of the cell large compared with the apparent rectifier resistance and with the resistance of the shunted measuring instrument. To illustrate this, scale readings corresponding to a range of conductances have been calculated and plotted in fig. 10. The maximum conductance C_x shown as abscissa is 300 micro-mhos (3333 ohms), an apparent resistance R_r of the rectifier, of 300 ohms and a resistance R_s of the shunted galvanometer, of 400 ohms (800 ohms for the instrument and 800 ohms for the shunt) were assumed. The smallest value for the ratio between the resistance of the cell and that of the rectifier was thus slightly over 10, for that between the resistance of the cell and that of the instrument slightly under 9. The scale readings are entered on the left of the diagram, 100 representing 4 microamperes. Five ranges corresponding to different values of the compensating P.D. E_b have been calculated and the positions of the points entered on the diagram. Points for the same value of E_b are connected by continuous lines, and it will be seen that these do not deviate perceptibly from straight lines. The currents I_m passing through the cell and rectifier have been entered as broken lines, their values in microamperes being shown on the right of the graph. The compensating P.D.s E_b corresponding to the pairs of lines indicated by the Roman figures

I to V were respectively 1·70, 2·35, 3·0, 3·65, and 4·30 volts. The value assumed for the corrected main P.D. E_m was 1·25 ($E_m' = 1·75$, $a = 0·5$), that for the resistance R_b was 15,000 ohms.

Numbers of experimental determinations with other values of E_m and E_b have been carried out by D. C. Lee, and
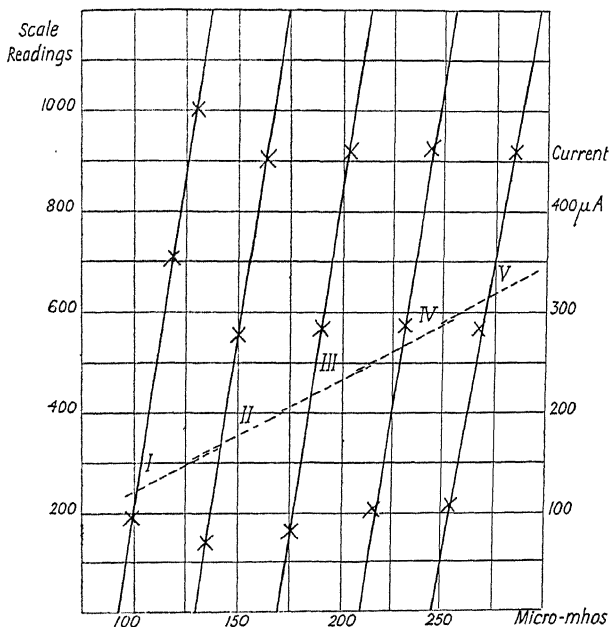
Fig. 10.—Lee's Circuit: Scale Readings and Conductances

similar straight lines have been obtained. The apparatus was successfully employed in the titration of sulphate (p. 59). It was constructed essentially of radio fittings. The test cell was of the pattern shown in fig. 3 (p. 64), and the galvanometer was a unipivot instrument of the type repeatedly referred to, having a resistance of about 800 ohms and giving a full-scale deflection for 24 microamperes. All the units

excepting the test cell and the galvanometer were combined
to form a single assembly or " set ", so that before using the
apparatus it was only necessary to plug into the A.C. mains
and connect up the two units mentioned. The method of
working with an unknown solution was as follows. The test
was started with the respective sliders set so as to make the
resistances between A and B, between D and E, and between
G and H zero. Slider B was then moved until a suitable
current between 200 and 1000 microamperes was obtained,
as already explained. The position of the sensitivity slider D
was then set so that the maximum change of conductivity to
be expected during the titration would give a deflection
covering as much of the scale as possible. The needle of the
galvanometer was now brought to a convenient position by
adjusting the bias slider H, and the titration was proceeded
with.

Valve Circuits.

A valve circuit employing grid rectification which allows
changes of conductivity to be followed by readings of the
anode current was described by Treadwell and Paoloni
(*Helv. Chim. Acta*, 1925, **8**, 89). The circuit is analogous to
that used with metal rectifiers, inasmuch as the cell is placed
in series with what is virtually an A.C. microammeter of
relatively low resistance. This is obtained by shunting a
valve-voltmeter circuit across the ends of a suitable resistance.
An interesting development of conductimetric valve circuits
is the " triodometer ", which is a combined oscillator and
valve ammeter employing a single valve (U. Ehrhardt, *Chem.
Fabrik*, 1929, **2**, 443, 455, 463). It is obvious that the use
of valves involves more complications than that of metal
rectifiers.

Conductivity Micro-titrations.

The fact, already discussed, that conductivity titrations are
independent of the reaction being quantitative at the equival-
ence point, makes them particularly suited to micro-titrations,
and much useful work in this direction has been done recently

by Jander and his collaborators. As stated on p. 54, it has been estimated that precipitation titrations may be performed if the concentration of the titrate ions in the solution equals only ten times the solubility of the precipitate.

For micro-titrations all storage and other vessels must be made of resistant glass, and be well steamed out. Only water free from carbonic acid may be employed. In some titrations dissolved air must be expelled by nitrogen. The titration vessel usually has a diameter of about 25 mm. and a capacity of about 50 ml. For the smallest quantities, titration vessels of a total capacity of 5 ml. have been employed. The electrodes usually arranged as in fig. 2a (p. 63) are left unplatinized, as platinum black would absorb an appreciable proportion of titrate. The solution is usually stirred mechanically. Burettes for micro-titration have been discussed on p. 66. The strength of the titrant solutions must obviously be reduced to correspond with that of the titrate, and records of the use of solutions of about N/2000 strength are not uncommon. The electric circuit was either that of Jander and Schorstein (p. 70), or that of the synchronous alternator and commutator (p. 72). There appears to be no reason why a Mullard bridge with cathode-ray detector should not yield equally satisfactory results (p. 69).

The following is a summary of the more important micro-titrations that have been recorded: arsenious acid by alcoholic iodine in amounts of 20 to 1 μg. (G. Jander and J. Harms, *Z. angew. Chem.*, 1935, **48**, 467); fluorine by aluminium chloride in the presence of sodium chlorate in aqueous alcoholic solution in amounts of 5000 to 50 μg. (J. Harms and G. Jander, *Z. Elektrochem.*, 1936, **42**, 315); lead, cadmium, copper, silver, and bismuth by hydrogen sulphide in quantities down to 1 μg. for the first four metals, and in quantities down to 10 μg. for the last-named (H. Immig and G. Jander, *Z. Elektrochem.*, 1937, **43**, 207); chloride ion by means of silver nitrate in quantities down to 10 μg. in aqueous, and in quantities down to 1 μg. in alcoholic solution (G. Jander and H. Immig, *Z. Elektrochem.*, 1937, **43**, 211).

Conductimetry of Solutions containing high Concentrations of Extraneous Electrolytes.

It was mentioned on p. 59 that high concentrations of extraneous electrolytes reduce the accuracy of conductivity titrations. This is due to the fact that most of the current is carried by the extraneous electrolytes, and the change brought about by the titration forms only a small fraction of the total conductance. Thus not only greater accuracy in the electrical measurements, but particularly closer temperature control is necessitated. If, for example, we assume the conductance due to the foreign electrolytes to be a hundredfold that due to the titrate, and the latter to change by 50 per cent as a result of the titration, then a change of 1 per cent in the total conductance, which might be brought about by a temperature change of, say, half a degree, would be twice as great as the change produced by the titration, and would completely swamp it. Nevertheless by carefully observing the precautions discussed on p. 66, and using the synchronous alternator and commutator referred to on p. 72, Jander and his collaborators have succeeded in determining small amounts of titrate ions in the presence of large amounts of foreign electrolytes. The titration cell was the circulatory vessel shown in fig. 4 (p. 65) with carefully platinized electrodes, the ratchet and wheel burette described on p. 66 being employed. Thus G. Jander and A. Ebert (*Z. Elektrochem.*, 1935, **41**, 790) have determined small quantities of perchloric acid in the presence of an excess of 500 equivalents of barium perchlorate by means of baryta, and similar small quantities of potassium iodide in the presence of a 500-fold excess of potassium nitrate by means of silver nitrate. J. Harms and G. Jander (*Z. angew. Chem.*, 1936, **49**, 106) have similarly titrated traces of phosphoric acid in the presence of a large excess of perchlorates with bismuthyl perchlorate, and G. Jander and H. Immig (*Z. Elektrochem.*, 1937, **43**, 214) have determined silver in the presence of an excess of about 500 equivalents of lead by titration with sodium chloride.

Literature on Conductimetric Analysis.

1. H. T. S. Britton: *Conductometric Analysis* (Chapman & Hall, 1934).

2. C. W. Davies: *The Conductivity of Solutions*, p. 234 (Chapman & Hall, 1933).

3. G. Jander und O. Pfundt: *Leitfähigkeitstitrationen und Leitfähigkeitsmessungen* (Enke, Stuttgart, 1934); also articles by G. Jander and O. Pfundt, and by K. Sandera in *Physikalische Methoden der analytischen Chemie*, part 2, ed. by W. Böttger (Akad. Verlagsgesellschaft, Leipzig, 1936).

4. I. M. Kolthoff: *Konduktometrische Titrationen* (Steinkopff, Dresden, 1923).

5. Also articles by J. Grant in *Industrial Chemist*, 1934, **10,** 350 and 391.

6. S. Glasstone: *Institute of Chemistry Lecture*, 1934 (*T.*).

7. T. Callan and B. Horrobin, *J. S. C. I.* (*T.*), 1928, **47,** 329.

Historical.

The following should be mentioned as pioneers in conductimetric analysis: F. Kohlrausch (1885), M. Berthelot (1891), F. W. Küster (1902), P. Dutoit (1910), I. M. Kolthoff (1920).

The Determination of Moisture by the Measurement of Capacitance (Dielectric Constants)

The determination of the dielectric constant or specific inductive capacity of a substance offers a rapid means for estimating its moisture content. Owing to the fact that the dielectric constant of water is about 80, whereas that of most other materials does not exceed 5, a small variation in water content may be expected to cause a large change in dielectric constant. The method has been applied to such materials as tobacco, grain, flour, tea, and other solids. Two modes of application are in use. In one the water is extracted by a suitable solvent, usually dioxan (L. Ebert and E. Waldschmidt, *Z. physikal. Chem.*, " Bodenstein Festband ", 1931, p. 101, and L. Ebert, *Z. angew. Chem.*, 1934, **47**, 305), and the change in dielectric constant of the solvent is determined. In the other, which is more rapid, and probably sufficiently accurate for most technical applications, the solid material itself is examined.

The Electrical Methods.

In all methods a condenser for holding the test substance is employed, and usually measurement is performed by means of the " substitution " method. In this a variable measuring condenser, set to a higher capacitance than the maximum to be expected from the test condenser, is placed in parallel with it in the circuit. The system containing the empty test condenser is first adjusted so that the indicating instrument, which may be a telephone, milliammeter, cathode-ray tuning

indicator, or other device, gives a certain indication, say a certain note for the telephone, a maximum current for the milliammeter, or zero P.D. for the tuning indicator. On introducing the test substance into the condenser, this indication is upset. It is then restored by reducing the capacitance of the measuring condenser by an amount equal to the increase caused by the test substance. This amount is thus the increase of capacitance to be measured. In actual practice a setting for the empty condenser need not be made every time. The moisture content to be determined may either be obtained from specially constructed tables or, alternatively, a scale showing moisture content may be applied to the instrument. In all present-day methods of measurement, alternating current is employed. Until comparatively recently frequencies much higher than 1000 cycles per second were not used. These may, however, be found insufficient when the test substance shows perceptible conductivity, and a frequency of the order of 10^5 to 10^6 cycles per second obtained from a radio-frequency oscillator is now commonly applied. A detailed discussion of methods is beyond the range of this treatise, and it is only possible to give here a survey of the more important principles involved.

The Wheatstone Bridge Method.

The Wheatstone bridge method was very generally employed before the advent of radio-technics. It is also used at the present time, e.g. in the humidity testers of the Cambridge Instrument Company, and there is little doubt that the employment of the cathode-ray tuning indicator (Vol. II, p. 5) as a null-point detector will greatly extend its range of usefulness in the future. The A.C. Wheatstone bridge method for liquids was developed largely by Nernst (*Z. physikal. Chem.*, 1894, **14**, 622; *Wied. Ann.*, 1897, **60**, 600). The bridge for measuring capacitances arises from that for measuring resistances, if two adjacent resistors are replaced by capacities. If one of these capacities, as is often the case, shows a small amount of conductance (leakage or power loss), it behaves as if a correspondingly high resistance had been

placed in parallel with it, and to obtain a sharp balance a corresponding high-resistance, non-inductive resistor may be placed in parallel with the capacity contained in the other arm, or a small resistance may be arranged in series with it. For a detailed account of the bridge method the reader is referred to a paper by A. O. Ball (*J. C. S.*, 1930, p. 570).

The Resonance Method.

In the resonance method a circuit is employed which contains inductance and capacitance, and is arranged for operating the substitution method (see above). This circuit is brought into resonance with oscillations provided by a valve oscillator lightly coupled with it, and giving a constant frequency of about 10^5 to 10^6 cycles per second. Resonance is indicated by a maximum anode current in a valve-voltmeter placed across the condensers. For descriptions of resonance circuits the reader is referred to papers by S. Sugden (*J. C. S.*, 1933, p. 768, and A. R. Martin, *Trans. Faraday Soc.*, 1937, **33**, 192).

Tuning to a Quartz Crystal.

In tuning to a quartz crystal use is made of the fact that a suitably cut quartz crystal will transmit electrical oscillations only of a certain characteristic frequency. The unknown and the standard capacities are introduced into the anode circuit of a quartz-controlled oscillator. When the capacitance is adjusted so that this circuit is in tune with the quartz crystal, there is a sharp fall in the anode current. The substitution method of measurement is employed. For a description of a quartz-crystal circuit the reader is referred to a paper by R. J. W. Le Fèvre (*Trans. Faraday Soc.*, 1938, **34**, 1127).

The Heterodyne Beat Method.

In the heterodyne beat method two loosely coupled high-frequency oscillators, producing, say, frequencies of 1000 and 1001 kilocycles per second are employed. One of these circuits contains the measuring and test condensers arranged for operating the substitution method. The beats are detected

by means of a detector circuit containing a telephone, either a standardized note or the merging of audibility into inaudibility being employed to locate the arbitrarily chosen number of beats. For a description of a heterodyne beat circuit the reader is referred to a paper by L. E. Sutton (*Proc. Roy. Soc.*, A, 1931, **133,** 668).

Condensers.

When liquids such as dioxan are being examined, a condenser may be employed, the plates of which consist of two stainless steel cylinders held concentrically with a gap of about 1 mm. by means of three glass rods. The assembly with its leads is rigidly held in a small cell resembling a Kohlrausch conductivity cell, from which it can be removed for purposes of cleaning. In use the liquid is filled to a fixed position in the cell and its water content is determined by means of a table which has been previously constructed for this purpose. For particulars about the construction of the cell the reader is referred to a paper by L. G. Groves and S. Sugden (*J. C. S.*, 1934, p. 1095), and one by Le Fèvre (*Trans. Faraday Soc.*, 1938, **34,** 1127).

For dealing with solids annular vessels are usually employed, which are packed with the test material to a fixed height, the apparatus being calibrated with similar material the moisture content of which is known from analysis by oven drying. In order to obtain comparable results, the same method of packing and the same grain size must as far as possible be employed in all tests on a given material.

Literature.

For an account of methods used in the measurement of dielectric constants the reader is referred to Chapter III of C. P. Smyth, *Dielectric Constant and Molecular Structure* (Chemical Catalog. Co., Inc.), 1931.

The Potentiometric Determination of p_H

The definition of p_H by equations (2) and (2a) has been given in Vol. I, on p. 26, and its colorimetric measurement by means of indicators was described on pp. 37 to 44. The general theory of its potentiometric measurement by means of the hydrogen and of the quinhydrone electrode has been discussed on pp. 77 to 80, and on pp. 85, 86, 94, and 95. It remains mainly, therefore, to describe the apparatus and the practical details involved.

The Hydrogen Electrode.

In a hydrogen electrode gaseous hydrogen is brought into thermodynamic equilibrium with the hydrogen ions of the solution by means of platinum black. The latter acts catalytically, adsorbing the hydrogen, probably in an atomic condition. As a support for the platinum black a platinum wire of perhaps 0·3 mm. diameter and 1 cm. length or a small plate of gauze or foil of, say, 1 sq. cm. total area may be employed. Slow absorption of hydrogen by the platinum support is said to delay the attainment of equilibrium. Some workers therefore prefer to plate the electrode with gold before depositing the platinum black on it. The former is carried out by means of an approximately 1 per cent auric chloride solution with a current strength of a few milliamperes, after which the electrode is polished. For easy saturation of the platinum black and the liquid adjoining it, with hydrogen it is desirable that the coating should not be too thick. The method of depositing is that given on p. 64, but the total time of deposition should not exceed $1\frac{1}{2}$ minutes. As stated, the electrode

must not be allowed to become dry, and the platinized wire or plate is therefore always stored immersed in water or in a suitable buffer solution. The readings obtained by means of any one hydrogen electrode should be periodically checked against those of another, particularly if any difficulty shows itself in obtaining a sharp balance. This is necessary owing to the fact that platinum black may have lost its catalytic efficacy, or, as it is usually expressed, have become " poisoned " by contact with catalytic poisons such as certain alkaloids, ammonia, sulphides, cyanides, arsenic compounds, sulphur dioxide, &c. In this case the platinum black should be removed, if possible with a piece of moist soft cloth, and the underlying plate be thoroughly cleaned chemically, and then be replatinized. When a gold or a gold-plated support is employed, the deposit of platinum black may be removed by electrolysis in hydrochloric acid. Platinum black is sometimes replaced by iridium or by palladium black.

In order that the electrode may attain equilibrium rapidly with the test solution, it should hold a film of the latter which is periodically renewed by suitable motion. This fact should be borne in mind in designing an electrode vessel. Thus W. Mansfield Clark recommended the use of a special mechanically operated rocking apparatus (*J. Biol. Chem.*, 1915, **23**, 475). The same purpose may, however, be attained by simpler means. Of the numerous designs that have been successfully operated, we shall describe three that represent various types of application.

The Bailey Electrode.

The Bailey electrode (*J. Amer. Chem. Soc.*, 1920, **42**, 45) represents a type which is suitable for small amounts of test liquid, and which requires a minimum amount of hydrogen. The last-named is important when the p_H of the liquid depends on the presence in it of CO_2 or of any other gas which would be expelled by a current of hydrogen. It is also important when the test liquid tends to froth. The Bailey electrode is used particularly in physiological laboratories. From fig. 1 it is seen that the vessel consists essentially of a U-tube

expanded to a bulb of about 15 mm. at one end, the other holding a stopper or being left open for closing with the thumb. The electrode plate is visible slightly above the bend. It is of gold with a platinum wire connexion. The electrode is operated as follows. The test liquid is poured in at the open limb, and the vessel is then inclined so that the closed limb is filled and the liquid reaches a small way above the bend. The vessel is then inclined back until the closed limb is almost vertical, and a long narrow capillary jet through which hydrogen is slowly flowing is introduced. Sufficient hydrogen is collected to fill the closed limb. The vessel is now filled to the top with test liquid and closed. It is then rocked backwards and forwards for a few minutes so that the hydrogen may bubble past the platinized electrode from one limb to the other, until the electrode is completely saturated with the gas. Before opening and adjusting the level in the open limb, the level of liquid in the closed limb is adjusted just to cover the plate. Connexion to the standard electrode may now be made by means of an agar bridge as described on p. 30.
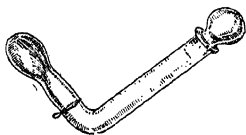
Fig. 1.—Bailey Electrode

The Lindsey Hydrogen Electrode.

The Lindsey electrode (*Analyst*, 1932, **57**, 573) is one of the best hydrogen electrodes of the enclosed type, the introduction and flushing out of the test liquid being simple, and the design of the hydrogen supply such as to ensure rapid saturation. The vessel is shown in fig. 2. The funnel limb A serves for filling and washing out the vessel, and also supplies the connexion to the reference electrode. The U-bend B acts as a trap to prevent entry of the junction liquid into the main vessel C. The hydrogen enters at D, is controlled by the stopcock E, and finally bubbles into the vessel at the orifice F, which is 2 to 3 mm. in diameter. The platinum electrode is supported in the neck G by means of a rubber stopper, and the hydrogen escapes from the trap H. When

the determination is complete, the stopcock I is opened and the liquid run away to waste. The vessel is washed out by filling the funnel A with water and then flushing away by opening the stopcock I. The hydrogen stream is adjusted to
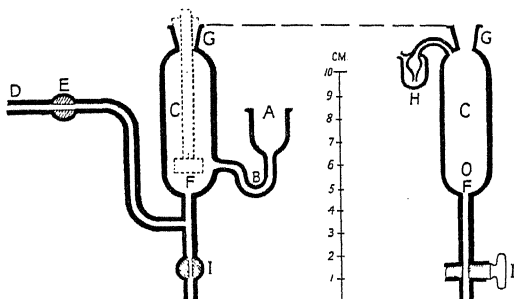
Fig. 2.—Lindsey Hydrogen Electrode

such a speed as to produce a pulsating movement of the test solution up and down the electrode, and can, if desired, be turned off during measurement. The amount of test solution required is 5 to 7 ml.

The Hildebrand Electrode.

The Hildebrand electrode referred to on p. 32 belongs to the bell type of electrode developed for purposes of potentiometric titration. As shown in fig. 3, it consists essentially of the platinum electrode proper, which is surrounded by an outer tube or bell into which the hydrogen enters through a side inlet, escaping at the bottom through the test liquid, which may be placed, say, in a small beaker. The feature which differentiates the Hildebrand electrode from the earlier electrodes used by the writer in conjunction with Wood and Law (p. 32), consists in the presence of four small holes near the bottom of the bell. When the speed of the gas is suitably adjusted,
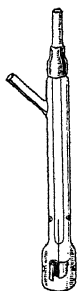
Fig. 3.—Hildebrand Electrode

this escapes at the bottom only, while test liquid running in through the side holes gives to the former an oscillatory motion. This, as explained, promotes rapid saturation of the electrode. In all bell pattern electrodes the gas stream must not be unduly decreased for reasons of economy.

Hydrogen.

Commercially obtained compressed hydrogen is usually sufficiently pure for use in hydrogen electrodes. It is generally bubbled through an alkaline solution of permanganate, and then passed through glass wool to remove spray. To avoid the annoyance of momentary high pressure on opening the valves, it is advisable to pass the gas through a safety T-tube, the open end of which dips into a few inches of water. A gas jar may be employed both to hold the water and to act as a support for the T-tube. When the hydrogen is prepared by the action of acid on zinc, it should be purified by passing through wash bottles containing mercuric chloride, alkaline pyrogallol, and alkaline permanganate.

The Quinhydrone Electrode.

The theory and application of the quinhydrone electrode and similar electrodes has been discussed on p. 34 and in Vol. I, p. 94. It is the simplest of any electrode used for p_H measurement, all the apparatus required being a small beaker into which an insulated platinum plate of about 1 sq. cm. area may be dipped. The test solution is poured into the beaker and enough quinhydrone to cover the tip of a penknife is stirred into the liquid. Connexion to the standard electrode is made either directly or by means of a connecting bridge (p. 29). As already stated (p. 34), the quinhydrone electrode cannot be employed in alkaline solution, the p_H limit being usually fixed at about 8. Like the hydrogen electrode the quinhydrone electrode cannot be used in the presence of oxidizers.

The Palladium Hydride Electrode.

The palladium hydride electrode, introduced by P. Nylen in 1937 (*Z. Elektrochem.*, 1937, **43**, 921) resembles the quin-

hydrone and other oxidation-reduction electrodes inasmuch as it reacts towards p_H like a hydrogen electrode of gaseous pressure different from atmospheric. Unlike the quinhydrone electrode, however, it may be employed in alkaline solution. Two identical electrodes are used, one as the test electrode, the other as the reference electrode. The latter is placed in a standard buffer solution. To prepare the electrodes, platinum wires or plates, such as are used as hydrogen or quinhydrone electrodes, are coated with palladium black. For this purpose they are first carefully cleaned with chromic or with concentrated nitric acid, and then well rinsed in water. They are now made cathodes in a bath of 1 to 2 per cent A.R. palladium chloride, acidified to approximately normal strength with hydrogen chloride, a voltage of about 4 being employed for about 4 minutes. To charge the electrodes with hydride, they are then polarized cathodically, using again 4 volts in approximately 10 per cent sulphuric acid for about a minute, rinsed in water and allowed to dry in the air. To make a pair of electrodes identical as regards hydride content, they are soaked in water for one or two minutes and then introduced into a test-tube containing approximately N/1 formic acid. Vigorous evolution of gas should take place after a few seconds. The electrodes are removed simultaneously from the formic acid after about two minutes, rinsed and placed in distilled water for three minutes. They are then introduced respectively into the test and buffer solutions, which are connected by an electrolyte bridge, the P.D. between them being measured. This P.D. should have become constant after 5 to 10 minutes. If it is indicated by E, the difference of p_H between standard and test solution is $E/0\cdot000198$ T, T being the absolute temperature.

Other Electrodes.

The *oxygen*, the *antimony*, and the *tungsten* electrodes have been discussed on pp. 33, 34 and 35. These electrodes should be specially calibrated by means of solutions of known p_H, and preferably of similar character to those to be tested. Thus the readings of the antimony electrode are dependent

on the concentration of dissolved oxygen. On account of its simplicity in use, the antimony electrode finds application in apparatus designed for recording and controlling p_H for industrial purposes. The reader is referred to a paper by P. Wulff, W. Kordatzki, and W. Ehrenberg (*Z. Elektrochem.*, 1935, **41**, 542) for a discussion of the antimony electrode.

Standard Electrodes and Bridges.

For housing the reference electrode required, any type of standard electrode vessel may be used. For the description of an electrode vessel, and for the charging of the saturated calomel electrode reference is made to Vol. II, pp. 34 and 44 respectively. The potassium chloride crystals recommended on p. 45 for use in the presence of foreign electrolytes may be omitted. For electrolyte bridges reference is made to pp. 29 and 30.

Potentiometers.

The chain consisting of the hydrogen or other similar electrode and the standard reference electrode with or without a separate connecting bridge having been set up, it remains to measure the P.D. between the terminals. For this purpose a potentiometer is required. Where no great accuracy is needed, the potentiometer described in Vol. II, p. 38 (fig. 29), may be employed. As a rule potentiometer boxes specially constructed for p_H measurement, and sometimes referred to as " ionization potentiometers ", are used. The diagrammatic fig. 4 explains the circuit commonly employed. The current from the large accumulator B passes successively through the adjustable rheostat M, the rheostat T, tapped as explained below, by the lead W_1, and then from P to Q through a series of equal, accurately adjusted resistances, at the end of any one of which the arm y_1 can make contact, thus providing the tapping Y_1. After Q, the current passes through a uniform wire RS, fitted on a drum, from which a tapping Y_2 can be taken by means of a slider y_2, and then back to the battery B.

The resistance between the points R and S must be accurately equal to each of the series resistances between P and Q.

This is readily attained by choosing the wire RS so as to have a slightly greater resistance than that required, and placing in parallel with it an appropriate shunt z. The circuit also contains a tapping W_2 at the position marked 0·4 after the tenth of the series resistances between P and Q. In ordinary use the current passing through the potentiometric circuit is adjusted so that the P.D. between two successive studs is accurately equal to 0·1 volt. Under such circumstances the
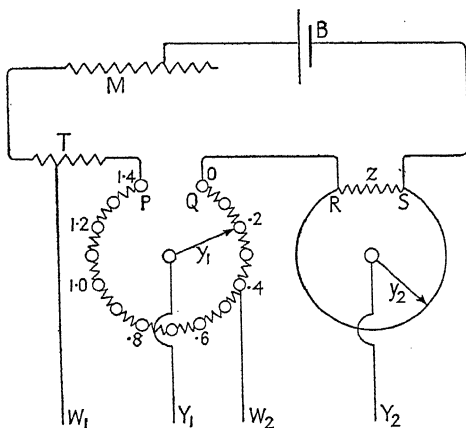
Fig. 4.—Ionization Potentiometer

potential difference between the tappings Y_1 and Y_2 can be read directly on two dials, one indicating tenths of a volt, the other the remaining fraction to one-tenth of a millivolt. To standardize the voltage of the potentiometer the E.M.F. of a Weston cell is balanced by means of a galvanometer against the P.D. between W_1 and W_2. The resistance of the potentiometric circuit between W_1 and W_2 must therefore stand in the same ratio to that between two successive studs, as does the E.M.F. of the Weston cell, viz. 1·0183 volts to 0·1 volt. Thus, if the resistance between two successive studs is 2 ohms, the resistance between P and the origin of

the tapping W_1 must be adjusted to 0·0366 ohm. In some potentiometers the position of W_1 is fixed, in others it is made variable in order to allow the use of different standard cells. The potentiometer is provided with a selector switch by means of which either W_1 and W_2 can be connected across the standard cell plus galvanometer, or Y_1 and Y_2 can be connected across the galvanometer plus the P.D. to be measured. Terminals are provided for connecting the galvanometer, the Weston cell, and one or more P.D.s to be measured to the potentiometer box. Many ionization potentiometers contain a fitting explained by fig. 4a which increases the sensitivity tenfold, while reducing the range to one-tenth.
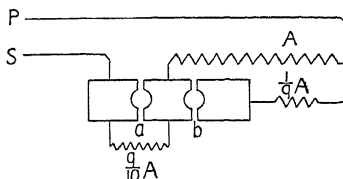
Fig. 4a.—Fitting to increase Sensitivity

For this purpose the P.D. between the points P and S must be reduced to one-tenth of its value, at the same time the current must remain unchanged, and therefore if we indicate the resistance between P and S by A, a resistance equal to $\frac{9}{10}A$ must be put in series with A, while it is shunted by a resistance equal to $\frac{1}{9}A$. A study of the figure will show that when a plug is placed at a, between the blocks shown, current passes directly through A, whereas when the plug is transferred to b, the total resistance remains unchanged, but only one-tenth of the current passes through A.

The Cambridge portable ionization potentiometer is a simplified form of the potentiometer just described. The galvanometer, which is of the unipivot type, is enclosed in the instrument, and serves not only as a zero instrument but also takes the place of the Weston standard cell. To set the instrument at the correct voltage, the stud-switch pointer corresponding to y_1 of fig. 4 is set to the position O, and the selector

switch to the " standardize potentiometer " position. The galvanometer plus a suitable series resistance is now shunted across two adjacent studs, corresponding to those shown between P and Q in fig. 4, which in this case represents a P.D. of 0·2 volt. The correct adjustment of this voltage is attained by means of a battery rheostat, when the needle of the galvanometer is opposite a red graduation provided on the scale. The potentiometer is now ready for use on setting the selector switch to the " test " position. The same instrument has been developed in another form for use with the antimony-saturated calomel electrode system. In this case the dials are calibrated to read p_H values directly at ordinary temperature.

Calculation of Results.

The equilibrium between gaseous hydrogen and hydrogen ions is expressed by the chemical equation $C11$ (Vol. I, p. 75). By applying to this the mathematical equation ($4a$) (p. 80, *ibid.*), substituting $\log[\text{H}^+] = -p_H$ and transposing, the equation is obtained,

$$E = E_0 - 0\cdot0000992\,\text{T}\log[\text{H}_2] - 0\cdot0001984\,\text{T}\,p_H \text{ volt, } (1)$$

in which E is the P.D. between the hydrogen electrode and the reference electrode (diffusion potentials being ignored), and E_0 the corresponding quantity, when all concentrations (respectively pressures) are equal to unity. Confining ourselves to the saturated calomel electrode, E_0 is the P.D. between the poles of a chain consisting of a hydrogen electrode under standard conditions ($p_H = 0$, $[\text{H}_2]$ = pressure of 1 atmosphere) and a saturated calomel electrode, which is obviously the negative value of e_{cal}, the P.D. sat. cal. — N/1 hydrogen electrode. The values for e_{cal} are contained in the following table:

Temp. °C.	18	20	25	30
e_{cal} volt	0·2506	0·2492	0·2464	0·2437

The effect of pressure is expressed in equation (1) by the term $0.000992 \log [H_2]$ in which $[H_2]$ is the pressure of the hydrogen gas in atmospheres. A barometric increase of 20 mm. or 0.026 atm. would make $[H_2] = 1.026$. Substituting this value and $T = 290$, we find the term $0.000099\, T \log [H_2]$ of equation (1) to be equal to 0.0003 volt, a quantity which we may neglect for ordinary purposes. Thus equation (1) gives the result

$$p_H = \frac{E_{cal-x} - e_{cal}}{0.0001984\, T}, \qquad (2)$$

in which $E_{cal-x} = -E$ is the measured P.D. between the saturated calomel and the test hydrogen electrode, and e_{cal} the potential of the saturated calomel electrode given in the above table. For ordinary temperature we make $0.000198\, T = 0.058$ volt.

When a quinhydrone electrode is substituted as test electrode for the hydrogen electrode we may employ equation (14b) (Vol. I, p. 95) for the calculation of p_H. Assuming the reference electrode to be the saturated calomel electrode, we have $E = -E_{cal-q}$, E_{cal-q} being the P.D. between the saturated calomel electrode and the quinhydrone electrode. The constant E_0'' of the equation quoted from Vol. I then has the following values: $E_0'' = 0.4538$ at $18°$ C. and $E_0'' = 0.4527$ at $25°$ C. We thus obtain at ordinary temperature

$$-\frac{E_{cal-q} + 0.454}{0.0580} \qquad (3)$$

To avoid the calculations arising from these equations, it is convenient to use a nomogram. A useful one which allows the ready conversion of hydrogen and quinhydrone voltages into p_H at various temperatures has been constructed by J. Grant and has been placed on the market by A. G. Gallenkamp Ltd. It is described in *J. S. C. I. (T.)*, 1930, **49**, 302. The reader is also referred to D. S. Davis, *A p_H Nomograph for Industrial Alkalies* (*Paper Ind.*, 1940, **22**, 802).

The Glass Electrode

The discovery that a potential difference depending on acidity exists between a glass membrane and an aqueous solution with which it is in contact was made by M. Cremer in 1906 (*Z. Biol.*, 1906, **47**, 562). F. Haber and Z. Klemensiewicz in 1909 (*Z. physikal. Chem.*, 1909, **67**, 385) showed that this potential difference varies with the hydrogen ion concentration of the solution similarly to the corresponding P.D. of a hydrogen electrode, and thus laid the basis for the technique of glass electrode measurement. These investigators employed a thin bulb of soft glass about a hundredth mm. thick, into which they introduced a solution of known hydrogen ion concentration. This was dipped into the test solution, and both solutions were connected to reference electrodes. The potential difference between the two reference electrodes was found to be given by the equation

$$E = K + 0 \cdot 000198 \, T \, p_H, \qquad (4)$$

where K is a constant. It might be expected that, when identical solutions and reference electrodes are employed inside and outside the bulb, then $K = 0$, or, if the reference electrodes are different, that K should equal their difference of E.M.F. This is, however, not accurately the case. A small anomalous P.D. amounting to a few millivolts and known as the " asymmetry potential " is always found. This asymmetry potential varies slightly with the hydrostatic pressure of the solution inside the bulb and tends to increase with increasing wall thickness. Its existence is no doubt due to a difference of strain on the two sides of the glass membrane. If kept low by the employment of a suitable glass of small enough wall thickness, it remains sufficiently constant during a series of measurements not to affect their accuracy.

The importance of the glass electrode lies in the fact that its indications are unaffected by the presence of oxidizing and reducing agents and poisons generally, that it is applicable

over a wide range of p_H, and that it comes to equilibrium almost at once. It suffers from the obvious disadvantage of very high resistance, but this difficulty has been largely surmounted by the use of modern methods of measurement.

Theory.

The variation of P.D. with p_H expressed by the above equation is explained completely by the assumption that the electrode acts as a "Donnan semipermeable membrane", which permits the passage of hydrogen ions while it is impermeable to other ions. Equally, the equation is explained by complete permeability of the membrane to hydroxyl ions only, or by permeability to both types of ions. This conclusion may be readily established either by direct thermodynamical reasoning or, say, by the application of equation (10) (Vol. I, p. 84), C_2 being made constant and $u_a = 0$.

Validity of the Equation.

In solutions of $p_H = 2$ to about $p_H = 9$ the equation given holds accurately. In more alkaline solutions deviations occur, which are dependent on the glass of the electrode and on the nature and concentration of the alkali present. These deviations are doubtless to be attributed to the fact that in the alkaline solutions electric charges are carried through the glass not only by hydrogen but also by alkali metal ions. According to K. Horovitz (*Z. physikal. Chem.*, 1925, **115**, 424), it is possible to construct glass electrodes the potential of which indicates concentrations of zinc, silver, and other metal ions.

The behaviour of glass electrodes in alkaline solution has been studied by numbers of investigators. We make special reference to the work of MacInnes, Dole, and Belcher, published mainly in the *Journal of the American Chemical Society* from 1930 onwards, to that of W. S. Hughes (*J. C. S.*, 1928, 491), and more recently to a paper by J. Powney and D. O. Jordan (*J. S. C. I.*, 1937, **56**, 133, *T*.), and one by D. O. Jordan (*Trans. Faraday Soc.*, 1938, **34**, 1305). The experimental conclusions may be summarized as follows. The deviations

of p_H from the linear relation given above depend on (a) the nature of the glass, (b) the nature and the concentration of the alkali or alkaline earth metal, (c) the temperature, and (d) the p_H of the solution. According to Powney and Jordan, the deviation Δ from the correct p_H which an electrode made of Corning glass (see below) shows in a solution of alkali ion of equivalent concentration m is reproducible, and is given by an equation of the form

$$\log \Delta = a p_H' + b \log m - c,$$

in which a, b, and c are constants and p_H' is the p_H calculated from the glass electrode potential, as if no deviation from the simple equation had occurred. The values given by Jordan for the constants a, b, c at 22° C. are contained in the following table:

	a	b	c
Sodium	0·540	0·46	4·20
Potassium	0·218	0·23	1·43
Strontium	0·275	0·50	1·98
Calcium	0·397	0·38	4·10
Barium	0·257	0·30	2·59

The constants a and c increase with temperature, whereas b is independent of temperature. Powney and Jordan (*loc. cit.*) showed that their results were in general agreement with an equation deduced on theoretical grounds by Dole (*J. Amer. Chem. Soc.*, 1931, **53**, 4260; also *J. Chem. Physics*, 1934, **2**, 862). According to S. J. Ssokoloff and A. H. Passynski (*Z. physikal. Chem.*, 1932, **160**, 366), deviations are small if the glass contains alkali metal of smaller atomic weight than that in the solution; thus a glass of the composition 10 per cent Li_2O, 10 per cent CaO, and 80 per cent SiO_2 is claimed to be suitable for measuring p_H values up to 12·5 in NaOH solution.

Composition of the Glass.

A considerable amount of work has been done to find a glass that has as low a resistance as possible, and at the same time gives readings agreeing with the simple theoretical

equation over as wide a range as possible. The glass recommended by D. A. MacInnes and M. Dole (*J. Gen. Physiol.*, 1929, **12**, 805) has the composition $Na_2O = 22$ per cent, $CaO = 6$ per cent, $SiO_2 = 72$ per cent. It is manufactured by the Corning Glass Company of New York. The glass previously recommended by W. S. Hughes was of similar composition, viz. $Na_2O = 20$ per cent, $CaO = 8$ per cent, $SiO_2 = 72$ per cent.

Other Properties and the Treatment of the Glass Electrode.

H. Kahler and F. de Eds (*J. Amer. Chem. Soc.*, 1931, **53**, 2998) point out that if a glass electrode membrane is not completely immersed in the test solution, a capillary film forms on the non-immersed portion, which may vitiate the results.

The glass prepared according to MacInnes and Dole probably contains water, for if the electrode is dried out, its resistance increases. This is in agreement with an observation by W. C. Johnson (private communication) that the resistance of a glass electrode may increase fifteen times as a result of annealing. Electrodes should therefore be stored in water or in a suitable buffer solution. There is a slight tendency for the glass to yield sodium ions to the test solution. According to E. G. Edwards and D. P. Evans (*J. C. S.*, 1937, 1938), the " alkaline drift " caused hereby in slightly buffered or unbuffered solutions is avoided if the test solution is stirred. Fresh electrodes are cleaned by prolonged treatment with chromic acid, then thoroughly rinsed and left in distilled water till required. Owing to variations in the asymmetry potential and consequent drift of the constant K, a glass electrode must be restandardized before use by means of a buffer solution of known p_H such as a $M/20$ potassium hydrogen phthalate solution of $p_H = 3.97$ at $20°$ C., or a $M/20$ borax solution of $p_H = 9.23$ at $20°$ C.

Design of Glass Electrode Systems.

The glass electrode now most frequently used is of the Haber bulb pattern. The other apparatus necessary is the receptacle

for the test solution and the standard electrode with its connecting system. Fig. 5 shows the Morton electrode system in which these items are assembled in a single unit (*J. Sci. Instr.*, 1930, **7**, 187). It is manufactured by the Cambridge Instrument Company. We propose to describe it in detail in order
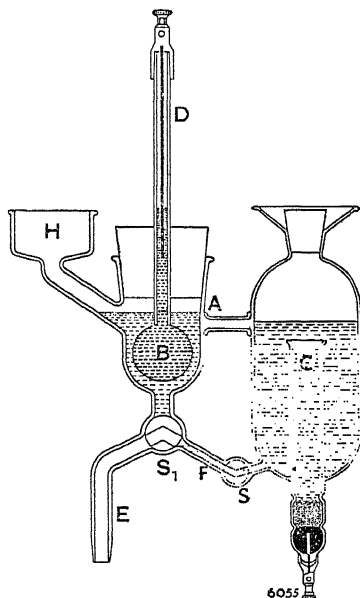
Fig. 5.—Morton Glass Electrode System

to furnish an example of the application of the glass electrode. The inside of the bulb B is developed as one of the two reference electrodes. A platinum wire dipping into a N/1 hydrochloric acid solution saturated with quinhydrone is employed in the older apparatus. It is being superseded in more recent construction by the more permanent Ag/AgCl, N/1 KCl electrode, in which the silver is a wire on which the solid silver chloride has been produced electrolytically. The other

reference electrode C is a saturated calomel electrode. It will be seen that the very high insulation necessary between the interior of the bulb and the rest of the system can be readily attained. The stem D should be made of a hard glass not likely to adsorb moisture, and it should be carefully freed from moisture by means of benzene, and dried with a clean cloth. Some workers prefer to coat part of it with paraffin wax. The test liquid is introduced into the vessel A through the cup H, and may be drained by turning the stopcock S_1. Liquid connexion to the saturated calomel electrode C is made past the closed stopcock S_1 through the tube F and the stopcock S. The stopcock S is greased completely, whereas only the top and bottom of the shank of S_1 are greased, a film of liquid round the centre being sufficient and essential in order to make connexion. The procedure recommended is as follows. The calomel electrode end of the system is first filled with saturated KCl solution up to the stopcock S, which is kept closed. The cup A, glass electrode, and drainage tube E having been rinsed with the test solution, the stopcock S_1 is opened to connect A with F, while stopcock S remains closed. A is then filled with the test solution. The stopcock S_1 having been turned to connect the calomel electrode vessel with the drainage tube, S is opened, and the system F, E flushed out with the KCl solution, a few drops being allowed to escape. The stopcock S_1 is kept closed during measurements. As explained above, the bulb B must be completely immersed, and when not in use the vessel A must be kept filled with distilled water or a suitable buffer. The figure also shows a glass strut near A fitted for mechanical reasons.

To protect glass electrodes from breakage they are frequently fitted with a shield. Another interesting suggestion for reducing fragility is based on experiments by M. R. Thompson (*J. Res. Nat. Bur. Stand.*, 1932, 9, 833). The interior of the glass electrode is first plated with silver, and then coated with copper electrolytically, so that electrical connexion can be made to it. The interior is then filled with paraffin wax or other suitable material. Electrodes based essentially on this principle have been put on the market by

the Jena works. They are of 3 cm. diameter, and as a result of employing a special glass, their electrical resistance is stated to be so low that they may be used with an ordinary potentiometer in conjunction with a pointer galvanometer in cases where an accuracy of $0 \cdot 1$ p_{H} is sufficient. In electrodes of the Thompson pattern it appears that the silver coating acts as a solution of definite p_{H} in conjunction with the glass. Such electrodes may be expected to require frequent standardization, if confidence is to be placed in their indications.

Another electrode the resistance of which is so low that it may be used with an ordinary potentiometer and galvanometer has been recently described by W. C. Johnson (*Chem. and Ind.*, 1939, **58**, 573). It is manufactured by Baird & Tatlock. The electrode consists of a bundle of capillary tubes closed at the end at which they dip into the test liquid and sealed with a wax cement into a wider tube of about 1 cm. diameter. It is shown in fig. 6 mounted in its electrode vessel. The figure is largely self-explanatory. The test liquid is introduced through the funnel on the right. Connexion between the test liquid and its reference electrode is made by a rubber tube of small bore fitted to the right arm below the tap, while the liquid in the capillary tubes which forms part of the other reference electrode is introduced by pouring it above the open ends of the tubes, then evacuating and releasing the vacuum. For earlier suggestions to reduce the resistance of the glass electrode, we refer among others to G. R. Robertson (*Ind. Eng. Chem. (Anal.)*, 1931, **3**, 5) and D. A. MacInnes and D. Belcher (*Ind. Eng. Chem. (Anal.)*, 1933, **5**, 199).

Fig. 6.—Glass
Electrode Vessel

An older important method for producing glass electrodes of relatively small resistance, and particularly of small dimen-

sions suitable for micro-work is due to D. A. MacInnes and M. Dole (*Ind. Eng. Chem. (Anal.*), 1929, **1**, 57). The procedure is as follows. A tube of suitable glass is blown to a bulb thin enough to show interference colours. A piece of this is sealed to the end of an ordinary glass tube by heating it to red-heat, causing a piece of the thin membrane to adhere, and then pressing the membrane down while heating gently, until complete adhesion is obtained. The application of the electrode is the same as that of the Haber bulb. Electrodes of this construction form part of the " Stadie electrode " system which is used in the examination of blood serum, and in which quantities down to 0·5 ml. may be examined without loss of CO_2 at blood temperature (W. C. Stadie, H. O'Brian, and E. P. Lang, *J. Biol. Chem.*, 1931, **91**, 243).

Another suggestion for measuring the p_H of very small amounts of liquid has been recently made by Y. Kauko and L. Knappsberg (*Z. Elektrochem.*, 1938, **44**, 261). They employ the Haber bulb, which is moistened completely with the test solution. In some experiments the electrode was surrounded with gauze, in others it was left bare. The connexion to the standard electrode system is made by means of a strip of filter paper or by a thread containing either the test solution or saturated KCl solution.

This section should not be concluded without a reference to the Kerridge glass electrode, which has played an important part in earlier research (*Biochem. J.*, 1925, **19**, 611, and *J. Sci. Instr.*, 1926, **3**, 404). In it the glass electrode plays also the part of a receptacle for the test solution, which makes it suitable for work with small quantities of liquid.

The Measurement of Glass Electrode Potentials.

The difficulty inherent in the measurement of glass electrode potentials lies in the high resistance of the membrane, records of which vary from under 1 to about 100 megohms. Most of the older measurements were carried out with the aid of quadrant electrometers which were either used as direct reading or as null-point instruments. Another method adopted was to connect the P.D. to be measured to a large

condenser, and to estimate the charge received by it after fixed periods by means of the throw of a ballistic galvanometer.

These methods have now been superseded by the use of the thermionic valve. Fig. 7 illustrates the principles involved in glass electrode potentiometers, less important details being omitted. The P.D. of the glass electrode system E is balanced against that of a potentiometer P, so that the P.D. of the combined system between the points G and H is
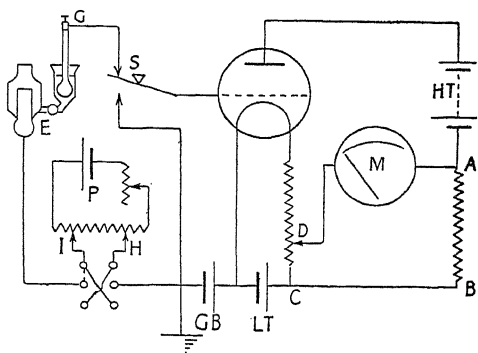
Fig. 7.—Glass Electrode System with Thermionic Valve

zero. It may therefore be interposed or removed from the grid circuit of a valve by means of the Morse switch S without affecting the anode current of the valve, and is shown in the diagram thus interposed. When the switch S is depressed, we have the ordinary valve circuit comprising the anode battery H.T., the filament battery L.T., and the grid-bias battery G.B. The system is designed so that a slight alteration in the grid bias, produced by interposing the glass electrode-potentiometer system in an unbalanced condition, will cause a large alteration in the anode current.

To use the circuit the potentiometer is balanced in the usual manner against a Weston cell. Switch S is then depressed, and slider D is moved until the galvanometer M shows no

current on depressing its galvanometer key (not shown). When this is the case, the ratio of anode to filament current is obviously equal to the ratio of resistance CD to resistance BA. The filament current remains constant; any alteration of the anode current produced by altering the grid bias will therefore cause a deflection in the galvanometer. On releasing the switch S, the electrode-potentiometer system is interposed, and the potentiometer dials are moved, until the galvanometer again shows zero current. The reading of the potentiometer is then equal to the E.M.F. of the electrode system. If the Morton glass electrode system is being used, viz. the system saturated calomel/test solution/glass membrane/ N/1 HCl, quinhydrone, then if the p_H of the test solution is varied from 0 to 12, the P.D. of the system will vary from about —0·45 volt to about +0·25 volt, passing through 0 at a p_H of about 7·75. For lower p_H values than this I must therefore be negative to H; for higher values it must be positive. A reversing switch is therefore interposed between the potentiometer and the glass electrode system as shown, or else the potentiometer is designed so that the P.D. between I and H can pass continuously from negative to positive values.

The p_H of the test solution is calculated by equation (4) of p. 99. In this the constant K depends on temperature and is approximately equal to —0·45 volt for the Morton system at ordinary temperature. To obtain its accurate value a buffer solution of known p_H is employed as explained on p. 93. It must be remembered that if the equation is used in the form we have given, E is the P.D. between the terminal of the calomel electrode, and the terminal leading to the interior of the glass electrode bulb. If E is defined in the opposite direction, a negative sign must be placed before the term containing the p_H of the solution.

Electrometer Valves.

Although glass electrodes are made which have a resistance of less than 1 megohm, high-resistance membranes are often used, and it may be necessary to be prepared for a resistance of about 10^8 ohms. The grid circuit of the valve should then

have an impedance of about 10^{10} or 10^{11} ohms, in order that the potential of the glass electrode may not be lost to the grid. This is considerably more than is to be found in ordinary valves. If the grid of a valve be kept sufficiently negative to the filament, current between the two is carried only by positive gaseous ions, and it is the minute conductivity produced by these that must be avoided in " electrometer valves ". In addition, therefore, to extremely high insulation of the grid, the use of a dull emitting filament, a low anode potential, and the shielding of the valve from light and from electrostatic influences by means of a metallic shield are called for in the construction and operation of an electrometer valve. In the General Electric Company's (Gt. Britain) Osram Electrometer type " T " valve the filament and anode are placed close together, and the grid is situated outside the direct path between them, the sequence being anode, filament, grid. With such an arrangement there is a minimum of ionization, and besides, the filament will tend to collect any positive ions that may have been formed (see G. B. Harrison, *J. C. S.*, 1930, p. 1580). For a description of this valve the reader is referred to G. W. Warren, *G.E.C. Journal*, May, 1935, or to a special pamphlet issued by the G.E.C. In another type of electrometer valve the grid is protected from positive ions by a positively charged screen grid (Metcalf and Thompson, *Phys. Rev.*, 1930, **36**, 1489).

Insulation of the Circuit.

A study of fig. 7 shows that the very high resistances of the circuit occur between the test solution and the interior of the glass electrode on the one hand and between the grid and the filament on the other, and that great care must therefore be taken to have the insulation of the part of the circuit between the interior of the electrode and the grid as perfect as possible. Other portions of the circuit are also of high resistance, and it is useful to earth the containers of apparatus and also the circuit itself at the position shown.

Circuits for Simplified and Routine Measurements.

In recent times apparatus for simplified working has been designed. As an example we take the Cambridge Direct Reading p_H meter suggested by C. Morton which is shown in fig. 8. In this instrument all the apparatus is supplied suitably mounted in a single case, and not only measurements in volts but also direct readings calibrated in p_H units at arbitrary temperatures may be made. The circuit is given in
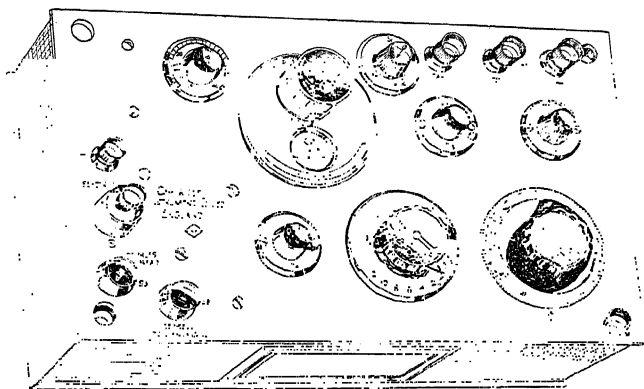
Fig. 8.—p_H Meter suitable for use with Glass Electrodes, Antimony, &c.

fig. 9. Of the switches shown, S_1 selects between p_H units and volt readings, S_2 between measurements on the test solution and the standardization of the potentiometer. We consider the circuit with the switches set as shown in the diagram. Starting from the positive pole of the battery, the circuit divides into two branches, one of which passes through a resistance corresponding to BA of fig. 7 and thence to the anode of the valve and the filament, where it rejoins the other branch. This latter branch passes through a resistance R_3 corresponding to CD of fig. 7 to the filament, and then successively through the resistance R_2, the potentiometer, and the battery rheostat R_1 back to the negative pole. The potentio-

meter is shunted by the resistance R_4, a slider corresponding to one of the two sliders H and I of fig. 7 being placed on the potentiometer proper, the other slider on the shunt R_4. By moving this slider the zero point of the p_H scale can be shifted without altering the magnitude of a p_H graduation. Obviously the slider on the potentiometer can be made either positive or negative to that on R_4, so there is no need here for a reversing switch such as that shown in fig. 7. The slider on the potentiometer is connected to two dials. This may be done
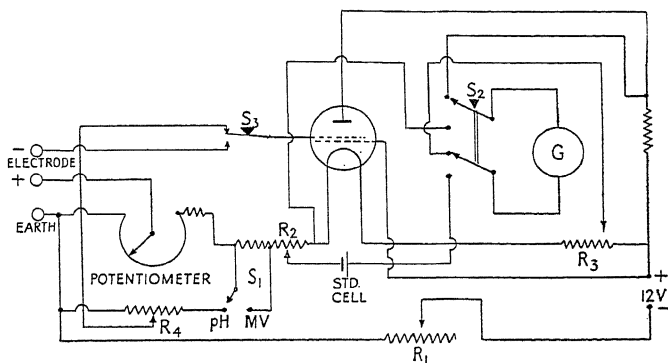
Fig. 9.—Circuit for p_H Meter of fig. 8

by the Kelvin-Varley slide method described in books on practical physics (e.g. Glazebrook's *Dictionary of Applied Physics*, Vol. II, p. 615). Provision must be made for altering the P.D. between the end-points of a graduation owing to the fact that the ratio between p_H change and P.D. change alters with temperature. A slider on R_2 is therefore provided. When this is set to its proper position on the " temperature compensating scale ", it determines the resistance correctly between two points of the circuit, whose P.D. should balance the E.M.F. of a Weston cell. It will be noted that in the diagram the grid of the valve shown is protected by a screen grid connected to the positive pole of the battery.

Another modern innovation is the introduction of p_H

meters working from the A.C. supply mains. In these the current is rectified, smoothed, and then stabilized by neon lamps as in modern radio receivers before use in the potentiometric circuit. The Marconi-Ekco p_H meter (*Ind. Chem.*, 1938, p. 412) belongs to this type. A feature of the instrument which deserves special mention is the amplification of the off-balance current by means of a three-stage valve amplifier. To make this practicable, the off-balance P.D. is interrupted at fairly high frequency by means of a motor-driven microswitch. The amplified A.C. obtained is rectified by means of a synchronous reversing switch before passing through the detecting instrument. For the latter a galvanometer of the robust milliammeter type is taken. Another feature is the automatic compensation for temperature necessitated by the change of slope of the p_H P.D. curve with temperature which has been referred to above. This compensation is made by means of a resistance, which is shunted across the potentiometer proper. The resistance, which changes with temperature, is disposed in a bulb immersed in the test solution, and thus automatically alters the ratio between the P.D. across the potentiometer and the E.M.F. of the standard cell.

In concluding this section we must refer to automatic recorders of p_H. In many cases the apparatus not only records but also controls the p_H of liquids by operating valves for the admission of acids and alkalis. A detailed discussion of these developments is, however, beyond the scope of this book.

The Determination of p_H by the Titration of Buffer Solutions.

The determination of p_H by the titration of buffer solutions appears to have been first suggested by G. Roeder (*Lait*, 1934, **14**, 904; also a pamphlet published by Dr. N. Gerber's Söhne of Zurich). In the operation of this method the test solution is connected with a comparison solution by means of an electrolyte bridge. Both solutions contain identical indicator electrodes for p_H, usually quinhydrone electrodes, and these are connected by a null-point instrument which

may be a capillary electrometer or a galvanometer. The comparison solutions are acids of known concentration, which are titrated with CO_2-free standard NaOH solution. The percentage neutralization of the acid at any instant is thus known, and its p_A value being also known, the p_H of the comparison solution may be calculated at any stage of the titration by means of equation (22b) (Vol. I, p. 45). The p_H of the test solution obviously has the value of that of the comparison solution, when the null-point instrument shows no P.D. between the indicator electrodes. The acid solutions chosen were those of formic and acetic acid, and potassium dihydrogen phosphate. To avoid the trouble of calculation burettes were supplied for each acid on which p_H values were read directly. The method has the virtue of great simplicity, while it retains the advantage of electrical over colorimetric methods of being independent of colour, salt error, &c. No temperature correction is required, since test and comparison solution have the same temperature.

This method has been operated by A. J. Lindsey in the writer's laboratory with the Britton and Robinson buffer mixture as supplied by Baird and Tatlock (see Vol. I, p. 48). A table was calculated by means of which p_H values between about 2 and 12 can be read from the volume of 0·2N sodium hydroxide required. According to this table, the buffer solution has a p_H of 4·60 after the addition of 22·4 ml. of 0·2N NaOH. Beyond this, the titration follows a strictly linear course till a p_H of 8 is reached, 1 ml. 0·2N NaOH being equivalent to an increase of p_H of 0·0852. For determinations with a slightly improved universal buffer see W. C. Johnson and A. J. Lindsey (*Analyst*, 1939, **64**, 490).

Historical.

The importance of acidity in enzyme catalysis was clearly recognized by Kjeldahl in 1881 (*Compt. rend. Trav. Lab.*, Carlsberg, 1881, **1**, 186), and also by O'Sullivan and Tompson (*J. C. S.*, 1890, **57**, 834). The fundamental rôle of hydrogen ion concentration was, however, established by Sörensen in 1909 (*Études enzymatiques II, Compt. rend. Trav. Lab.*,

Carlsberg, 1909, **8**, 1 and 396; also *Biochem. Z.*, 1909, **21**, 131, 201; **22**, 352). To Sörensen we owe the recognition of the exponential relation between hydrion concentration and effectiveness of catalysis in biological processes, and also the introduction of the p_H function (exponent or " power " of hydrion concentration). Since Sörensen's first paper the applications of p_H determination have grown beyond measure, and the reader is referred to the larger treatises for an account of these.

The idea of a buffer solution was introduced by Fernbach in 1900. In a study of the catalytic activity of malt extracts he realized the importance of the primary and secondary phosphates contained in them in keeping the acidity of the solution between the limits in which it acts alkaline to methylorange and acid to phenol phthalein. He likened the effectiveness of the phosphates in resisting the results of small additions of strong acids and alkalis to that of a buffer in withstanding mechanical shocks (French, *tampon*) (A. Fernbach and L. Hubert, *Compt. rend.*, 1900, **131**, 293). Numerous buffer solutions have been described by Sörensen, Mansfield Clark, and others.

Literature.

We refer to the following books:

1. H. T. S. Britton: *Hydrogen Ions*, 2nd ed. (Chapman & Hall, 1931).

2. J. Grant: *The Measurement of Hydrogen Ion Concentration* (Longmans, Green & Co., 1930).

3. W. Mansfield Clark: *The Determination of Hydrogen Ions*, 3rd ed. (Baillière, Tindall & Cox, 1928).

4. L. Michaelis: *Hydrogen Ion Concentration* (Baillière, Tindall & Cox, 1926).

5. E. B. R. Prideaux: *The Theory and Use of Indicators* (Constable & Co., Ltd., 1917).

6. H. Jörgensen: *Die Bestimmung der Wasserstoffionen Konzentration* (Steinkopff, Dresden, 1935).

For a full discussion of the Glass Electrode we refer to M. Dole's book: *Principles of Experimental and Theoretical Electrochemistry* (McGraw Hill, 1935).

Supply of Special Apparatus.

Special apparatus described in this treatise may be obtained from Messrs. Griffin & Tatlock Ltd. of Kemble Street, W.C., and branches. Other apparatus described in the book is also obtainable from them as well as from other firms of dealers.

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